

The University of Chicago

THE ELECTROMOTIVE FORCE OF
THE CELL $\text{Pt}, \text{H}_2, \text{HCl}, \text{AgCl}, \text{Ag}$,
WITH EXTREMELY DILUTE
ELECTROLYTE

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
JUNE, 1934

By
NELSON JAY ANDERSON

CHICAGO, ILLINOIS

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INTRODUCTION

To obtain thermodynamic data for aqueous solutions of hydrogen chloride more dilute than 0.01 molal, the cell $\text{Pt}, \text{H}_2, \text{HCl}, \text{AgCl}, \text{Ag}$, has been used by Noyes and Ellis,¹ Linhart,² Nonhebel,³ Roberts,⁴ Carmody,⁵ and Harned and Ehlers.⁶ The results of their investigations contain some discrepancies which have been attributed to adsorption, to impurities, and to the reaction of the acid with glass containers. Carmody's work⁷ was very carefully done and his results are undoubtedly excellent for the range of concentrations he included, but he stated that his apparatus was not suitable for measurements with solutions more dilute than about 0.0003 molal. Linhart⁸ and Nonhebel⁹ have each reported two values of electromotive force for solutions more dilute than 0.0003 molal, but their values are not in good agreement. Linhart¹⁰ considered his value for his lowest concentration (0.000136 molal) as somewhat unreliable. With this solution in his cell, he observed that, for a period of 105 hours during which hydrogen was continually flowing through the solution, the electromotive force changed from a maximum value of 0.6798 volt to

¹Noyes and Ellis, J. Am. Chem. Soc., 39, 2532 (1917).

²Linhart, J. Am. Chem. Soc., 41, 1175 (1919).

³Nonhebel, Phil. Mag. (7) 2, 1085 (1926).

⁴Roberts, J. Am. Chem. Soc., 52, 3877 (1930).

⁵Carmody, J. Am. Chem. Soc., 54, 188 (1932).

⁶Harned and Ehlers, J. Am. Chem. Soc., 54, 1350 (1932); 55, 2179 (1933).

⁷Loc. cit.

⁸Loc. cit.

⁹Loc. cit.

¹⁰Loc. cit.

0.6697 volt. Nonhebel¹ reported that attempts were made to measure electromotive forces with solutions more dilute than 0.0001 molal, and that the attempts were unsuccessful because the electrodes would not come to equilibrium.

Güntelberg² obtained experimental evidence which showed that it is necessary to exclude oxygen from the cell used for electromotive force measurements. He explained how oxygen caused error by its participation in a side reaction represented by the equation,



This reaction reduces the hydrogen chloride concentration and the electromotive force becomes higher than that which corresponds to the concentration of the solution put into the cell. To avoid this source of error, Güntelberg³ passed oxygen-free nitrogen through the solution used in the silver-silver chloride half cell, and since his work was reported, other experimenters have taken precautions to keep oxygen away from the silver-silver chloride electrodes. Güntelberg suggested that the side reaction represented by the equation,



may take place if hydrogen gas is present in the portion of the cell containing the silver-silver chloride electrode. To avoid this suspected source of error, he used a cell constructed so that hydrogen was excluded from that part of the cell. Pearce and Fortsch⁴ had previously observed that silver deposits upon

¹Loc. cit.

²Güntelberg, Z. Physik. Chem., 123, 199 (1926).

³Ibid.

⁴Pearce and Fortsch, J. Am. Chem. Soc., 45, 2852 (1923).

the platinum cathode in the cell, Pt, H₂, HI, AgI, Ag.

Kraus and Parker¹ showed that the concentration of an aqueous solution of a strong acid (more dilute than 0.005 molal) changes when the solution stands in glass containers. To this suspected source of error, M. Randall and L. E. Young² have attributed the discrepancy between the results of electromotive force and freezing point measurements.

Investigators have not agreed that any one type of silver-silver chloride electrode is the best or that different types are equally good. Several different forms of the electrode have been used. MacInnes and Parker³ plated silver at low current density upon platinum gauze in an aqueous solution of potassium silver cyanide, and the silver chloride was plated upon the silver by electrolysis in an aqueous solution of hydrogen chloride. Noyes and Ellis⁴ varied this method by using two layers of silver. The first layer was deposited electrolytically from an aqueous solution of potassium silver cyanide upon a platinum helix. The second layer was formed from silver oxide paste which filled the helix and which was heated until only silver remained. Upon the silver, Noyes and Ellis⁵ plated silver chloride by electrolysis in an aqueous solution of hydrogen chloride. They stated that this was the only type of silver-silver chloride electrode, among forms that were tried, that gave satisfactory results. Harned and Ehlers⁶ and Roberts⁷ used this type of electrode. Linhart⁸

¹Kraus and Parker, J. Am. Chem. Soc., 44, 2429 (1922).

²Randall and Young, J. Am. Chem. Soc., 50, 989 (1928).

³MacInnes and Parker, J. Am. Chem. Soc., 37, 1445 (1915).

⁴Loc. cit.

⁵Ibid.

⁶Loc. cit.

⁷Loc. cit.

⁸Loc. cit.

and Gerke¹ used finely divided silver prepared electrolytically at high current density in an aqueous solution of silver nitrate. A layer of silver chloride prepared metathetically was placed upon a layer of the silver. Güntelberg² reported that he obtained better results with electrodes prepared according to the method of Noyes and Ellis³ than he did with the electrodes of the type used by Linhart⁴ and Gerke.⁵ Carmody⁶ did not accept any of the electrodes used by earlier experimenters. He plated platinum gauze with silver from a cyanide solution, washed for five days, and finally formed a layer of silver chloride electrolytically. The electrodes which he used were white. Some brown ones obtained were discarded. These he found to be about 0.2 to 0.3 millivolt positive with respect to the white ones.

The purposes of this research grew out of an interest in the variations of procedure and the diversity of the results of former investigators, especially in the variation of the time required for the cells to come to equilibrium. The voltage of some of Linhart's⁷ cells (and some of the cells studied in the early part of this research) varied for 100 hours or more; whereas, voltage readings were accepted by some investigators from one to five hours after the hydrogen had begun to flow through their cells. Nonhebel⁸ reported that equilibrium was reached in three hours. Carmody⁹ found that equilibrium was attained in four

¹Gerke, J. Am. Chem. Soc., 44, 1684 (1922).

²Loc. cit.

³Loc. cit.

⁴Loc. cit.

⁵Loc. cit.

⁶Carmody, J. Am. Chem. Soc., 51, 2905 (1929).

⁷Loc. cit.

⁸Loc. cit.

⁹Loc. cit.

hours. Roberts¹ found that constant potentials were reached within one or two hours. Noyes and Ellis² do not mention the amount of time required before their first reading was taken, but they reported measurements taken for five to eight hours after the first one was made. Linhart³ observed the variation of the voltage of the cell containing his most dilute solution (0.000136 molal) for 105 hours, but he believed that equilibrium had been reached by that time. It seemed that many, if not all, of the electromotive force data of former investigators might be in error. Five hours might appear to be a sufficient time for equilibrium to be attained in some particular experiment, but during this time, side reactions might occur to such an extent that the value of the electromotive force measurements would be destroyed. It seemed that an understanding of the cause of the variation in the time required for cells to come to equilibrium might lead to a satisfactory explanation for some of the disagreement in electromotive force data. An investigation of this problem might also result in an explanation of the failure of the data of all investigators (except Carmody⁴) to fit the limiting law predicted by the Debye-Hückel⁵ theory. Davies⁶ had concluded that solutions of hydrogen chloride do not conform to the Debye-Hückel⁷ theory (although other uni-univalent strong electrolytes do), but since Carmody's⁸ data appeared, Davies⁹ has reversed his original conclusion concerning solutions of hydrogen chloride.

¹Loc. cit.

²Loc. cit.

³Loc. cit.

⁴Loc. cit.

⁵Debye-Hückel, Phys. Zeits., 24, 185 (1923).

⁶Davies, "The Conductivity of Solutions," John Wiley and Sons, New York, 1930.

⁷Loc. cit.

⁸Loc. cit.

⁹Davies, J. Am. Chem. Soc., 54, 1698 (1932).

THE CAUSES OF THE TIME VARIATION OF THE ELECTROMOTIVE FORCE

In some preliminary experiments, as well as in some later ones, the following general results were observed. When hydrogen passed continually for at least one hundred hours through the electromotive force cell (Fig. 1) containing a dilute (less than 0.0005 molal) aqueous solution of hydrogen chloride, a gradual and continuous decrease in voltage followed an initial comparatively short period when the voltage increased (Figs. 2 and 4). There was a period of increase in the electromotive force for all solutions tried. This could be accounted for by such factors as the saturation of the solution with hydrogen and with silver chloride, the saturation of the platinum electrode with hydrogen, and the removal of air. The initial variation of voltage, which was to be expected, was not fully investigated in this research. During the period of decrease in the electromotive force, the voltage change was in the direction that would be expected if the hydrogen chloride concentration was increasing. When hydrogen passed through the cell for a sufficient length of time, silver deposited upon the platinum electrode in sufficient quantity to change its color from black to grey. When an electrode with the deposit upon it was dipped into nitric acid, the normal color of the platinized platinum was quickly restored. In one experiment, the solution was about 5×10^{-5} molal and after hydrogen had passed through it for only twenty-four hours, silver was dissolved from the platinum electrode and readily detected by the usual

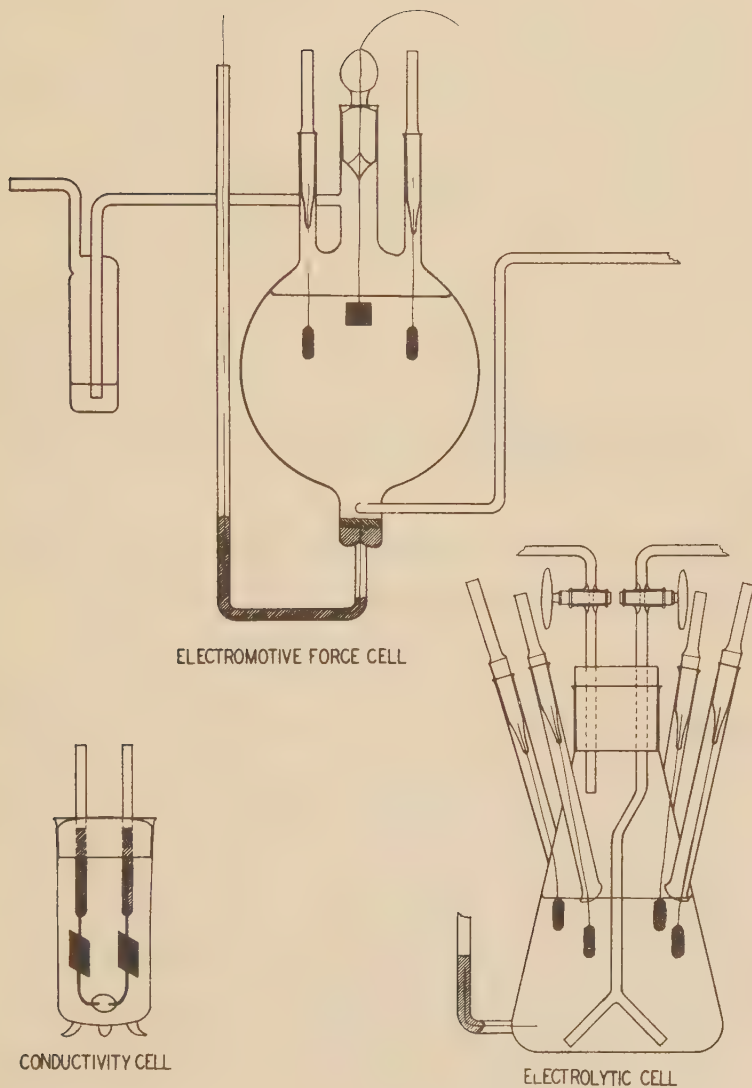


FIGURE I

qualitative method. In another experiment, the initial solution in the cell was an aqueous solution of hydrogen chloride about 5×10^{-6} molal (and dissolved silver chloride). For sixty-six hours, hydrogen was passed through the solution, in contact with which there was present an excess of silver chloride and a platinumized platinum electrode. The residual solution in the cell contained enough hydrogen chloride to yield easily a detectable precipitate of silver chloride when a little aqueous solution of silver nitrate was added though the solution in the cell at the start yielded no such precipitate. The electromotive force decreased during the sixty-six hours from a maximum value of 0.81555 to a final value of 0.64160. The maximum voltage was read about an hour after the hydrogen had begun bubbling through the solution in the cell.

When hydrogen passes through a sufficiently concentrated aqueous solution of hydrogen chloride there is no noticeable change in the electromotive force or in the conductance (see Fig. 2). In an early experiment, hydrogen passed through a solution 0.045 molal for a week, and no detectable silver could be dissolved from the platinum electrode by nitric acid. In this case, the voltage apparently remained constant for 110 hours after the maximum electromotive force was first reached.

In one experiment, the spiral type of electrode (Noyes and Ellis) and the layer type (Linhart) were simultaneously used in the cell containing an aqueous solution of hydrogen chloride 0.000221 molal. The methods of preparation of the electrodes will be described later. The curves of Figure 2 show the voltage variation for each of the two types of electrodes. The marked differences are evidences that the kind of silver-silver chloride electrode used is a factor of fundamental importance in the

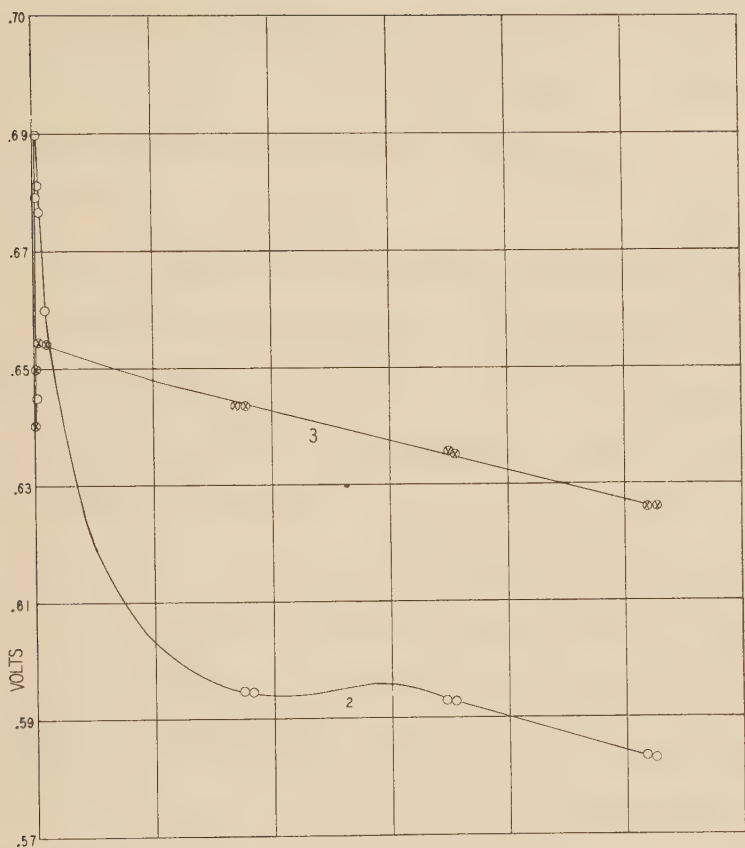
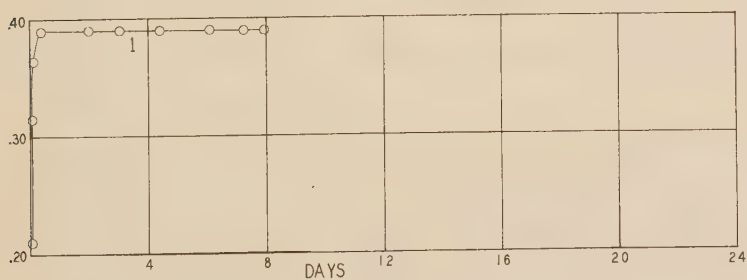


FIGURE 2

Time Variation of Voltage

Curve 1. HCl solution 0.045 molal, Linhart electrode.
 Curve 2. HCl solution 0.000221 molal, Linhart electrode.
 Curve 3. HCl solution 0.000221 molal, Noyes and Ellis electrode.



determination of the electromotive force.¹ Subsequent experiments showed that the Noyes and Ellis type of electrode gave consistent results; whereas, the Linhart type was not reliable in the very dilute solutions. No thorough investigation of this type was made. However, one experiment was made which should be recorded because it may eventually throw some light on the erratic behavior of the electrode.

In this experiment, the finely divided silver and silver chloride were thoroughly mixed, and the resulting mixture was placed in the electromotive force cell in lieu of the usual two layers. A solution of hydrogen chloride 0.1104_5 molal was used in the cell. The maximum electromotive force of the cell was about 0.18 volt higher than the expected value for a solution 0.1104_5 molal. But, when samples of the same silver and silver chloride were placed in layers, the electromotive force of the cell containing hydrogen chloride solution 0.1054_3 molal was 0.34981 volt, which is very nearly the expected value (within about 0.0002 volt). For solutions as concentrated as this, the layer type gave reasonably good results although Güntelberg found the Noyes and Ellis type better.

When a sample of the mixture of silver and silver chloride stood in a concentrated aqueous solution of nitric acid for an hour, scarcely any silver dissolved. A little of the mixture was shaken in an aqueous solution of ammonia and allowed to stand for half an hour, and most of the silver chloride dissolved. The solution was separated by decantation from the residual solid

¹In some recent investigations, Cowperthwaite, La Mer, and Barksdale (J. Amer. Chem. Soc., 56, 544 [1934]), and also Brown (J. Am. Chem. Soc., 56, 646 [1934]) have made studies of the silver-silver chloride electrode and have found that good results were obtained with dilute aqueous solutions containing chloride ion.

which then readily dissolved in nitric acid.

It was suspected that a contributing cause for the voltage variation might be some change in the hydrogen chloride concentration due to the removal of vapors by hydrogen when it passed through the solution at the usual rate of one liter per twenty-eight minutes. This possibility was tested by three experiments. Four saturators (see description of apparatus) were connected so that hydrogen must pass through them in succession before it entered the cell. Each saturator was initially filled with hydrogen chloride solution of the same concentration as that used in the cell. The electrical resistance of the solution remaining in each saturator and in the cell was measured at the beginning and at the end of each experiment. In Table I, the molalities calculated from the conductances are compared. The high molality of the solution remaining in the first saturator shows that the hydrogen, dry when it enters, removes vapor in which the mole fraction of hydrogen chloride is much less than its mole fraction in the solution. The residual solution in the second saturator had a molality only slightly higher than the one remaining in the fourth in which the concentration of the solution had not changed during the experiment. The solution remaining in the third saturator had a molality a little less than that in the second. Thus, hydrogen became nearly saturated with vapor in the first saturator and was so nearly saturated by the time it reached the cell that it could not change the concentration of the electrolyte in the cell during the experiment. These conclusions were confirmed by calculations with the equation,¹ $\frac{\sqrt{P}}{m} = K\gamma$. $K = 0.000664$, and $\gamma = 0.99$ at a molality of 8.623×10^{-5} . The results of the calculations are given

¹Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1933, pp. 330, 336, 337.

in Table II. For the solution 8.623×10^{-5} molal, the mole fraction of hydrogen chloride in the liquid phase is 10^7 times as great as it is in the vapor phase.

TABLE I

EXPERIMENTAL DATA SHOWING THAT HYDROGEN DOES NOT CHANGE THE CONCENTRATION OF HCl IN THE CELL BY VAPOR REMOVAL

Exp. No.	Initial m of HCl Solution	Final m of HCl Solution in Cell at End of Experiment	Final m of HCl Solution in First Saturator
I	0.00008623 ₂	0.0003160 ₄	0.00009328 ₅
II	.002087 ₀	.002174 ₂	.003468 ₂
III	.04642 ₃ [*]	.04645 ₀	.04895 ₄

Exp. No.	Final m of HCl Solution in Second Saturator	Final m of HCl Solution in Third Saturator	Final m of HCl Solution in Fourth Saturator	No. of Days that H ₂ Passed Through Saturators and Cells
I	0.00008633 ₄	0.00008630 ₀	0.00008626	27
II	.002094 ₂	.002090 ₆	.002088 ₃	47
III	.04720 ₀			8

*With the solution 0.04642 molal, only three saturators were used. The third one was a bubble tube.

After the elimination of the possibility that vapor removal was a cause of the variation of the composition of the solution, the reason for the variation was readily demonstrated to be the reaction between the silver chloride and the hydrogen as represented by the equation,



TABLE II

CALCULATED DATA SHOWING THAT HYDROGEN WOULD NOT BE EXPECTED TO REMOVE HCl FROM THE E.M.F. CELL

For Exp. No.	m_{HCl}	$m_{\text{H}_2\text{O}}$	$P_{\text{H}_2\text{O}}$	P_{HCl}	$\frac{P_{\text{HCl}}}{P_{\text{H}_2\text{O}}}$	$\frac{m_{\text{HCl}}}{m_{\text{H}_2\text{O}}}$
I	8.623×10^{-5}	55.51	3.094×10^{-2}	3.214×10^{-15}	1.039×10^{-13}	1.553×10^{-6}
II	2.087×10^{-3}	55.51	3.094×10^{-2}	1.810×10^{-12}	5.851×10^{-11}	3.759×10^{-5}
III	4.6423×10^{-2}	55.51	3.094×10^{-2}	7.025×10^{-10}	2.335×10^{-8}	8.363×10^{-4}

m_{HCl} = moles of HCl per 55.51 moles of H_2O (liquid phase).

$P_{\text{H}_2\text{O}}$ = partial pressure of H_2O in atmospheres from aqueous solution of HCl.

P_{HCl} = partial pressure of HCl in atmospheres from aqueous solution of HCl.

This was shown by two experiments, designated as No. I and No. II in Table III, where the results are given. Experiment No. I was carried out as follows. A solution of hydrogen chloride was prepared in the manner described later (see "Materials"). A weighed amount of the solution was introduced into the cell, the saturators were partly filled with some of the solution, the cell without electrodes was closed, hydrogen was passed through for two days, and the electrical resistance of the residual solution removed from the cell was measured. Then, after a layer type of silver-silver chloride (Gerke and Linhart) and the platinum electrode had been put into the cell, it was closed. Hydrogen was passed through the cell continually until it was opened to remove samples of the residual solution for a conductance measurement. When the cell was opened, the platinum electrode was removed; the silver was dissolved from its surface in a boiling solution of nitric acid, and quantitatively determined by the usual gravimetric

TABLE III

QUANTITATIVE EVIDENCE TO SHOW THAT A SIDE REACTION TAKES PLACE IN THE ELECTROMOTIVE FORCE CELL

Exp. No.	Molality of HCl Solution in Cell immediately Before Ag-AgCl Electrode Was Placed in the Solution	Amt. of Time of Flow of Hydrogen Between Initial and Final Resistance Measurements	Final Molality of HCl Solution Removed from the Cell		Change in Molality of HCl during the Passage of H ₂ Through the Cell, Determined by Conductance	Silver Equivalent in Grams	Silver Found on Pt Electrode in Grams
			Determined by Electro-motive Force	Determined by Conductance			
I ^a	$8.831_0 \times 10^{-5}$	28 days		$3.582_5 \times 10^{-4}$	$2.699_4 \times 10^{-4}$	0.0145_6^b	0.014#5
II ^c	$2.210_0 \times 10^{-4}$	20 days	$3.903_7 \times 10^{-4}$	$3.903_6 \times 10^{-4}$	$1.693_6 \times 10^{-4}$	0.00849	0.00818

^aHCl was used to precipitate silver chloride.

^bThe values in this column were calculated from those in the preceding one by multiplication by the appropriate gravimetric factor and by the number of kilograms of water in the solution used.

^cKI was used to precipitate silver iodide.

analysis involving silver halide.

Experiment No. II was carried out in the same way, except that, in addition to the layer type of silver-silver chloride electrode, a spiral type (Noyes and Ellis) was placed in the cell, and voltage measurements, including a final one just prior to the opening of the cell, were made. From the final voltage measurement, the concentration of the residual solution was calculated later by means of the equation,

$$0.118306 \log m\gamma = E_0 - E.$$

The value of γ used for the calculation represented in Table XII was calculated from equation (21). At the time the experiment was performed, this calculation was slightly less exact because equation (21) was not yet available.

In Table III, the results show the agreement between the molality calculated from conductance and the molality calculated from the electromotive force measurement. These data also show that the silver deposited upon the platinum electrode is chemically equivalent to the change in hydrogen chloride concentration.

The discovery of this side reaction marked a turning point in the progress of the research and, in spite of this obstacle, means were found to obtain electromotive force measurements for extremely dilute solutions. Former investigators had accepted electromotive force values obtained when equilibrium conditions had apparently been reached. The procedure of some of these investigators was to introduce a standard solution of hydrogen chloride into the cell, pass hydrogen through the solution, and wait for constant voltage readings. They assumed that equilibrium had been reached when the voltage remained apparently constant for an hour. This procedure is evidently successful when the solutions

of hydrogen chloride are not too dilute. But, it is unsatisfactory whenever the concentration of the hydrogen chloride changes appreciably during the period required for the voltage to become approximately constant.

It was suspected that the silver deposited upon the platinized platinum electrode might possibly in some way interfere with the normal functioning of the platinum as a hydrogen electrode. To test this possibility, the following experiment was performed. One platinized platinum electrode was partially submerged in the solution in the cell; another platinized platinum electrode was supported above the solution by a platinum wire extending through a hole in one of the glass stoppers of the cell, and held in position by a little paraffin in such a manner that the electrode could be forced down into the solution.

The solution which was put into the cell and into the saturators was 4.1×10^{-5} molal in hydrogen chloride. Hydrogen was passed through the cell for two days during which time several electromotive force measurements were made. After a final measurement was made by the use of the electrode that had been submerged in the solution, the other platinized platinum electrode was pushed downward into the solution and a reading of the potential difference between it and the silver-silver chloride electrode was made. The two readings were 0.72709 volt and 0.72712 volt respectively. The platinum electrodes were removed from the cell and each one was separately treated with an aqueous solution of nitric acid to dissolve any silver that might be present on its surface. The usual qualitative test showed that silver was dissolved from the platinum electrode which had been in the solution for two days; whereas, no detectable silver was found upon the other electrode. This experiment shows that silver upon the electrode does not

interfere with its normal functioning.

On account of the side reaction it is necessary to determine the concentration of very dilute hydrogen chloride solutions after the completion of the electromotive force measurements. If this is done, the side reaction causes no serious difficulty. It is necessary, however, to take elaborate precautions against errors due to adsorption and to consider the solubility of silver chloride in dilute solutions of hydrogen chloride. The details of the procedure adopted to avoid these sources of error are described below.

APPARATUS

In some of the preliminary experiments, it was necessary to use the type of cell which caused Linhart¹ and others trouble because one purpose was to find some explanation of the formerly observed variation of electromotive force with time. The same type of cell was used throughout since it possessed several advantages: (1) liquid junctions were avoided (although they probably produced only very small errors in such cells as the one used by Carmody²), (2) relatively large capacity for electrolyte was provided to avoid adsorption errors. The cell was made of transparent silica so that reaction of the acid with the glass would be avoided. In the early work, the hydrogen was passed through two wash bottles and through a three-bulb saturator very similar to the one used by Linhart.³ In later work, it was desirable to determine changes in the concentration of the solutions within the saturators and hydrogen was thereafter bubbled through four flasks, each one containing hydrogen chloride solution. The first three flasks were of Pyrex glass, the last one of transparent silica.

The cell designed and used for electromotive force measurements is shown in Figure 1. Its capacity was about 600 milliliters. Throughout most of the work it had three necks, two for silver-silver chloride electrodes of the spiral type, and one for

¹Loc. cit.

²Loc. cit.

³Loc. cit.

the platinum electrode. The layer type of electrode was in a pit at the bottom of the cell, into which a platinum wire extended from a tube used to make electrical contact by means of mercury. The cell was constructed entirely of silica, except for two soft glass stoppers in which the platinum wires leading to the silver-silver chloride were sealed. The lower terminals of these soft glass stoppers were far enough up inside the necks so that the soft glass did not come into contact with the liquid in the cell during an experiment. To support the platinum electrode, a tubular silica stopper, ground to fit the neck, was used. Above and below the ground surface, the stopper was constricted to the platinum wire which supported the 0.5 cm. by 0.5 cm platinum plate that served as the electrode. Platinum electrodes were prepared according to the directions given by Popoff, Kunz and Snow¹ except that no lead acetate was used in the platinizing solution. To seal the wire into the constricted silica, a little paraffin was used. Similarly, the platinum wire entering at the bottom of the cell to make contact with the layer type electrode was sealed into its tube with paraffin. The portion of this tube sealed to the pit of the cell was of quartz. It was extended by a glass portion sealed to it by means of a commercial cement² consisting of a mixture of materials containing cellulose produces and necessary solvent.

A quartz to glass graded seal connected the cell to a bubbler valve which permitted the hydrogen to escape from the cell and prevented the entrance of air. The bubbler contained a little solution of the same concentration as that of the liquid in the

¹Popoff, Kunz, and Snow, J. Phy. Chem., 32, 1056 (1928).

²"Glutex," Johnson and Co., Chicago.

cell. The exit tube from the cell extended into the liquid of the bubbler to a depth of 6.5 to 7.0 millimeters. The diameter of this tube was so large (4 millimeters) that it was not necessary to consider capillarity in the calculation of pressure.

The cell and the four saturators were supported on a metallic frame attached to a ring stand. Rubber cushions were used at all points of contact between the metal frame and the cell and saturators. When the cell was in use, it was covered by a layer of black cotton cloth to exclude light. Each saturator, having a capacity of about 300 milliliters, was made from a spherical flask. To the neck of each saturator two tubes were sealed directly opposite each other. One, used for entering gas, extended inside and nearly to the bottom of the flask; the other, used as an outlet for the gas, was sealed at the side of the neck. The first three saturators were sealed together with glass tubing, the third to the fourth with a Pyrex to quartz graded seal, and the last to the cell with quartz tubing. The transparent silica flask was used as the final saturator to obviate the influence of glass upon the electrolyte in the cell.

For the measurements of electromotive force, a type K potentiometer No. 102873 was used. This potentiometer was calibrated by a method similar to that recommended by Leeds and Northrup Company.¹ The details of the calibration procedure will be described later by Young and Hartsuch. For the values of the corrections, see Table XII.

An Eppley cell, No. 65778, was used in the potentiometer, the standard cell dial of which was adjusted to make 1.0189₂ volts the corrected reading of Eppley cell No. 70207. This value was

¹Bulletin 755, Leeds & Northrup Co., Philadelphia, 1929.

given by the Eppley Company for this cell at 22°C., June, 1932. Cell No. 70207 was calibrated by the United States Bureau of Standards just after the completion of this work, September 9, 1933, and its electromotive force was reported to be 1.0188₅ at 28°C.

A 2 volt lead storage cell was used to furnish the working current for the potentiometer. It was frequently necessary to adjust the working current by means of a slight change in the resistance of the circuit. The adjustment was made just prior to each electromotive force measurement and was tested immediately following the measurement. If an appreciable change had occurred the resistance was readjusted and the measurement repeated.

The galvanometer was a Leeds and Northrup, Type R. The characteristics of the galvanometer are: sensitiveness, 2327 mm/μa; critical damping resistance, 10,000 ohms; coil resistance, 580 ohms. A deflection of 2 mm. was produced in the galvanometer by a change of about 0.01 millivolt in the scale setting of the potentiometer when the concentration of the solution in electromotive force cell was 9.7×10^{-5} molal.

The galvanometer and the potentiometer rested upon metallic shields. These and the thermostat were all grounded by means of metallic contact between their supports and the plumbing system. The wire leads were supported from paraffined glass tubes suspended from a wire aerial which was grounded to the shields just mentioned. The galvanometer was protected by a timed iron cover equipped with a small window opposite the galvanometer mirror.

The thermostat contained Wenco C transformer oil sold by Westinghouse Electric and Manufacturing Company, Chicago. The thermostat was regulated so that the maximum variation in temperature was not greater than 0.02°C. All measurements of electromotive

force and of resistances of liquids reported in this paper were made at $25^{\circ} \pm .03$ C. The thermometer used in the thermostat was calibrated by comparison with a thermometer which had been calibrated at the United States Bureau of Standards.

The conductivity apparatus included a 1000 cycle microphone hummer (Leeds and Northrup), which produces nearly pure sine wave current, a resistance box, No. 32299, having a range 1 to 100,000 ohms, a resistance box, No. 120642, with a range of 1000 to 20,000 ohms (both resistances boxes contained coils of the Curtis¹ type), a Kohlrausch slide wire with end coils, No. 73441, a two stage radio amplifier, head phones, an air condenser, and a plug condenser, No. 33890. Lead covered copper wires, B. S. gauge No. 12, were used for leads and connections. All of the apparatus except the microphone hummer was mounted upon a double deck table. The A, B, and C batteries for the amplifier were placed upon the lower deck, and the other pieces upon the upper. The microphone hummer was placed in a felt padded box at a distance of ten feet from the bridge. Both the bridge and the box containing the microphone hummer were mounted upon metal sheeting. All of the lead sheaths of the wire leads and connections were grounded directly to the metal sheeting, as was also the midpoint of the Kohlrausch slide wire. The leads from the bridge to the thermostat terminated in glass U-tubes fastened about one foot apart at the side of the thermostat. The U-tubes were partially filled with mercury, and they were connected with the terminals of the conductivity cell with copper wires. The arrangement A, described by Schlesinger and Reed,² was used in the bridge. Jones and Josephs³ found that

¹Curtis and Grover, Bur. Standards Bull. Sci., Vol. 8, No. 3 (1912), p. 455.

²Schlesinger and Reed, J. Am. Chem. Soc., 41, 1727 (1919).

³Jones and Josephs, J. Am. Chem. Soc., 50, 1049 (1928).

a shield for the assemblage of apparatus used in the Wheatstone bridge introduced capacitances in such quantities that they were greater sources of error than the inductances which are present when no shield is used. No shields were used except the lead coverings of the insulated copper wires. A two-stage audio-frequency amplifier was connected between the bridge and the head phones. The plug condenser was connected in parallel with the head phones since it was found to increase the sharpness of the minimum. One or two small auxiliary air condensers were connected in the bridge when it was found necessary to balance out small capacitances. The points at which it was necessary to connect a condenser were easily determined by trial. It was not necessary, and in fact it might have been an objectionable procedure, to change the points of connection for the small auxiliary condenser during any one experiment in which two or more solutions were compared.

The silica conductance cell (Fig. 1) had a volume of about 75 cc. It was a cylindrical cup having a diameter of about 3 cm. The ground silica stopper was marked so that it could always be set in the same position in the mouth of the cell. Two tubes were sealed into the stopper and each one contained a heavy platinum wire (1 mm. in diameter). Paraffin was used to complete the seal between the platinum wires and their containing silica tubes. A platinum electrode about 1.4 cm. by 1.4 cm. was welded to the lower terminal of each wire. To the lower edge of each electrode was welded a short piece of the same platinum wire. These were sealed by the use of paraffin into small cups at the opposite ends of a short piece of silica. High melting (47°-49°C.) paraffin,¹ special filtered, was used to make the seals. This paraffin did

¹The Coleman and Bell Co., Norwood, Ohio.

not spread so as to change the resistance in the cell. The arrangement maintained the electrodes in constant positions during the ordinary processes, such as cleaning and filling.

To change the distance between the electrodes, the heavy platinum wires supporting the electrodes were bent. The equation, $R = \frac{160 \sqrt{d}}{A}$, proposed by Parker¹ was used as a guide to determine the approximate distance between the electrodes. The electrodes were cleaned and platinized according to the recommendations of Popoff, Kunz, and Snow² except that the gold plating process was omitted.³ One pair of electrodes which were gold plated did not function properly.

A copper wire cage covered with black cotton cloth to exclude light was used to support the conductivity cell in the oil in the thermostat, and was placed at such a depth that the mouth of the conductivity cell was one-half inch above the surface of the oil.

Immediately before the resistance of a solution was measured, the resistance of a coil in the auxiliary resistance box No. 120642, having approximately the same resistance as that of the solution, was measured by means of the conductivity apparatus. In this way, it was demonstrated that the apparatus was consistently yielding results reproducible to 0.01 per cent. Jones and Josephs⁴ showed that a source of error in measurements made by means of the Wheatstone bridge is introduced by the use of a ground wire connected to the midpoint of the Kohlrausch slide wire. But, the error was eliminated, at least so far as relative values of approximately equal resistances are concerned (absolute

¹Parker, J. Am. Chem. Soc., 45, 1366 (1923).

²Loc. cit.

³No lead acetate was used in the platinizing solution.

⁴Loc. cit.

values of resistances are not needed in our work), because the resistances in the resistance box were adjusted so that the balance point on the slide wire was quite near the center (the "500 position"). The mercury, used in the glass U-tubes at the side of the thermostat and in the tubes of the conductivity cell to make electrical contact with the bridge, was kept clean. It was shown by experiment that mercury standing for some time in these tubes changes resistance sufficiently to be appreciable, possibly due to film of dirt. It was occasionally necessary to clean the insulated surfaces of the resistance box used in the bridge and of the one used as an auxiliary. A cotton cloth moistened with alcohol was used for this purpose.

The resistance box, No. 3229, used in the Wheatstone bridge was calibrated by a procedure outlined in Table IV. Only relative values of the resistances of the coils in the resistance box were required. The equation, $\frac{R_1}{R_2} = \frac{4500 + S}{5500 - S}$, was used to calculate the unknown resistance from a known resistance and a slide wire reading. R_1 and R_2 are the resistances, S is the slide wire reading.

An ordinary mercurial barometer, Cenco type of Central Scientific Company, Chicago, was used. To determine the instrument correction (Table XII) for the barometer, it was compared with a standardized barometer used at the local weather bureau. The two barometers were hung side by side for a week, during which time comparative readings were taken. To serve as a guide for the position of the eye in reading the barometer, an iron rod was supported in a fixed horizontal position perpendicular to the mercury column.

Two analytical balances were used. The smaller one was adjusted so that it had a sensitivity of 4.0 scale divisions per

TABLE IV

CALIBRATION DATA FOR RESISTANCE BOX NO. 32299 USED
IN THE WHEATSTONE BRIDGE

- I. The 1000 ohm (face value) coil of resistance box No. 120642 was used as the standard resistance in the Wheatstone bridge to measure each 1000 ohm (face value) coil in the 1000 ohm dial of resistance box No. 32299. The results are tabulated as follows:

No. of Each 1000 Ohm Coil (face value) in Order in 1000 Ohm Dial of Resistance Box No. 32299	Slide Wire Reading	Relative Values in Ohms of Resistances of Coils in 1000 Ohm Dial of Resistance Box No. 32299
1	499.5	1000.20 ₀
2	499.6	1000.16 ₀
3	499.6	1000.16 ₀
4	499.6	1000.16 ₀
5	499.6	1000.16 ₀
6	499.6	1000.16 ₀
7	499.6	1000.16 ₀
8	499.5	1000.20 ₀
9	499.4	1000.24 ₀

- II. The 1000 ohm (face value) coil of resistance box No. 120642 was used as the standard in the Wheatstone bridge and the coils in the small dials, 1, 10, and 100* of resistance box No. 32299 were measured as a unit. Slide wire reading = 499.5; relative value of the total resistance of all coils in three dials = 1000.2₀₀ ohms.
- III. The sum of the relative values of the coils in dials, 1, 10, 100 and 1000 of resistance box No. 32299 = 10001.8₀ ohms.
- IV. The coils taken together as a unit in dials, 1, 10, 100 and 1000 of resistance box No. 32299 were used as a standard in the Wheatstone bridge and the 10,000 ohm (face value) coil of resistance Box No. 120642 was measured. Slide wire reading = 499.5; relative value of the 10,000 ohm coil = 9999.2 ohms.

*The resistances of the most concentrated solutions were small enough to be measured entirely by the coils in the 1, 10, and 100 dials, but errors in these coils cancelled because, in every case, the calibration solution had nearly the same resistance as the solution of unknown molality.

TABLE IV--CONTINUED

V. The 10,000 ohm coil (relative value 9999.1₂ ohms) of resistance box No. 120642 was used as the standard resistance in the Wheatstone bridge and each 10,000 ohm (face value) coil in the 10,000 ohm dial of resistance box No. 32299 was measured. The results are tabulated as follows:

No. of Each 10,000 Ohm Coil (face value) in Order in 10,000 Ohm Dial in Resistance Box No. 32299	Slide Wire Reading	Relative Values in Ohms of Resistances of Coils in 10,000 Ohm Dial of Resistance Box No. 32299
1	496.5	10011.2 ₀₄ ^{**}
2	492.75	10028.2 ₃₈
3	491.7	10032.4 ₅₁
4	499.0	10003.1 ₉₉
5	494.0	10023.2 ₂₅
6	492.3	10030.0 ₄₄
7	493.6	10024.8 ₂₉
8	496.3	10014.0 ₀₈
9	494.3	10022.0 ₂₃

^{**}The coils in the 10,000 ohm dial were not used except in the measurement of the resistance of conductivity water.

mg. at a 100 g. load. It was used to weigh loads less than 150 g. The large balance was adjusted so that its sensitivity was 0.5 scale divisions per mg. at 1500 g., and it was used to weigh loads greater than 150 g. The "method of swings" was used in all weighings. All weights were calibrated by the method of Richards.¹

¹Richards, J. Am. Chem. Soc., 22, No. 3, 144 (1900).

MATERIALS

To prepare hydrochloric acid, the best quality of sulfuric acid (Baker's Analyzed) was slowly introduced by means of a dropping funnel into a generating flask upon crystals of sodium chloride (Baker's Analyzed) and the resulting hydrogen chloride was absorbed in conductivity water (specific conductance not greater than $0.95 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$). The apparatus employed was similar to that used by H. C. Parker.¹ The hydrogen chloride, before it was adsorbed by water, was dried by the use of concentrated sulfuric acid and phosphorous pentoxide respectively. By means of a graded seal, a piece of silica tubing about twenty centimeters long was sealed to the end of the glass delivery tube through which the hydrogen chloride was delivered into the receiving silica flask. This precaution was used to avoid possible action of hydrochloric acid upon glass and the inclusion of the resulting impurities in the standard solution. The delivery tube extended through a cork stopper in the neck of the flask and down to a point about three millimeters above the surface of the water. The flask was in a beaker covered with a wooden lid. Thus, while absorption of hydrogen chloride gas was taking place, no dust settled upon the surface of the flask to cause error in the value of its weight. From the weights of the empty dry flask, of the flask and added water, and finally of the flask and hydrogen chloride solution, the concentration of the solution was determined. This

¹Parker, J. Am. Chem. Soc., 45, 2017 (1923).

analysis was checked by the usual gravimetric method¹ involving silver chloride.² In this way, two primary standard solutions of hydrogen chloride were prepared, and samples of them were used in the preparation by dilution of all of the secondary standard solutions. The required calibration solutions were prepared by the dilution of samples of the secondary standard solutions (see Table VI). The results of the analyses of the primary standard solutions of hydrogen chloride are given in Table V.

TABLE V

MOLALITIES OF PRIMARY STANDARDS

- (a) The molality of the primary standard solution No. I as determined by absorption of HCl was 2.549₃.
- (b) The molality of the primary standard solution No. I as determined by the precipitation of AgCl (sample I) was 2.549₆.
- (c) The molality of the primary standard solution No. I as determined by the precipitation of AgCl (sample II) was 2.550₂.

The average molality of standard solution No. I was 2.549₇.

- (d) The molality of the primary standard solution No. II as determined by absorption of HCl was 2.074₃.
- (e) The molality of the primary standard solution No. II as determined by precipitation of AgCl (sample I) was 2.074₀.
- (f) The molality of the primary standard solution No. II as determined by precipitation of AgCl (sample II) was 2.075₄.

The average molality was 2.074₇.

The conductivity water was prepared by the distillation of a dilute solution made from ordinary distilled water and

¹Fales, "Inorganic Qualitative Analysis," The Century Co., New York.

²Analyses involving silver chloride or silver iodide were carried out in dim artificial light. Silver iodide was involved in only one analysis mentioned later.

TABLE VI

GENESIS OF STANDARD SOLUTIONS OF HCl
EXPRESSED IN MOLALITIES

Primary Standards	Secondary Standards	Tertiary Standards	Quaternary Standards
2.074 ₇	0.01255 ₅₈	2.236 ₇ x10 ⁻⁴	0.2963 ₂ x10 ⁻⁴ *
		1.398 ₇ x10 ⁻⁴	
		0.9540 ₆₇ x10 ⁻⁴	
2.549 ₇	0.02556 ₂	36.53 ₂ x10 ⁻⁴	0.2963 ₂ x10 ⁻⁴ *
		0.5119 ₂ x10 ⁻⁴	
		0.6053 ₃₈ x10 ⁻⁴	
	0.1136 ₂	7.209 ₇ x10 ⁻⁴	0.2963 ₂ x10 ⁻⁴ *
		3.874 ₂ x10 ⁻⁴	
	0.5011 ₅	29.50 ₈ x10 ⁻⁴	
		19.45 ₇₈ x10 ⁻⁴	
		12.08 ₇ x10 ⁻⁴	
		8.947 ₆ x10 ⁻⁴	

*The tertiary standards were calibration solutions except this one.

alkaline potassium permanganate. About 5 grams of potassium permanganate and 10 grams of sodium hydroxide were added to fifty liters of distilled water. This volume is the approximate capacity of the available conductivity water still which has a copper reservoir provided with a block tin condenser and delivery tube. The solution was heated in the conductivity water still until distillation began. Then the heat was shut off and the solution was allowed to stand in the still over night. During the next day, conductivity water was collected in Pyrex glass bottles, four to ten liters in capacity. Only the middle portion (about one-half

of the total distillate) was accepted. During the process of the collection of conductivity water, considerable steam continually issued with drops of water from the end of the delivery tube so that very little carbon dioxide or other ingredients of the air were included in the water collected in the receiving bottle. Conductivity water prepared in this way had an initial specific conductance ranging from $0.55 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$ to $0.75 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$, but after it had stood in contact with clean air, its specific conductance rose to approximately $0.9 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$ and remained at this value in contact with the air.

Two types of silver-silver chloride electrodes were used: the layer type and the spiral type. The layer type of electrode was prepared and placed in the cell in a manner similar to that used by Linhart.¹ The materials for the layer type electrode were prepared as follows.

Silver was first precipitated by the addition of a pure aqueous solution of silver nitrate (Baker's Analyzed) to a pure aqueous solution of ammonium formate (Baker's Analyzed). The precipitated silver was washed by decantation, by the use of cold distilled water at first, followed by repeated washings with hot distilled water.

From the precipitated silver, a bar of pure silver was prepared by the fusion of the finely divided metal in a porcelain boat lined with pure calcium oxide. In preparation for the fusion of the silver, the boat was first filled with a paste made from calcium nitrate and conductivity water. When the boat filled with this material was heated in an electric furnace, a good lining of calcium oxide remained. The boat was then filled with finely

¹Loc. cit. See also, Randall and Young, loc. cit.

divided silver which was fused in the electric furnace. More silver was added and the process of fusion was repeated until a silver bar of the approximate dimensions $0.5 \times 1 \times 6$ cm. was obtained. The bar, after it had been washed in an aqueous solution of nitric acid and then in water, was ready for use as anode in the electrolytic preparation of finely divided silver. The bar of pure silver was made the anode in a pure aqueous solution of silver nitrate, and a platinum wire was the cathode. A current of one-half ampere to six amperes was used; the particular current density used in any particular preparation depended upon the type of experiment in which the electrode of silver and silver chloride was to be used.

The silver chloride used to prepare the layer type of electrode was produced by metathesis. Pure silver nitrate, prepared by recrystallization of Baker's Analyzed silver nitrate, was added to hydrochloric acid which was the middle portion of the distillate from reagent quality of acid. The chloride was thoroughly washed to remove impurities.

The finely divided silver and the silver chloride were each allowed to stand for at least an hour in several portions of an aqueous solution of hydrogen chloride, of the same concentration as that to be used as electrolyte in the cell. First, a layer of the silver was put into the cell, and upon this layer the silver chloride was introduced.

To prepare the spiral type of silver-silver chloride electrode, a platinum wire four or five inches long was boiled for a short time first in nitric acid and then in an aqueous solution of sodium hydroxide. After the wire was thoroughly washed in distilled water, it was heated in the Bunsen flame until it imparted no color to the flame. One end of the wire was sealed into the end of a piece of soft glass tubing so that electrical contact

could be maintained by the use of a little mercury in the tube. The other end of the wire was made into a spiral with an internal diameter of about one millimeter and a length of about eight millimeters. The spiral was dipped into moist silver oxide to fill the space within it and to cause to adhere to the outside of it a layer of the oxide thick enough to obscure the platinum. The spiral with adherent silver oxide was baked in an electric oven at 400°C . to 450°C . for three hours to reduce the oxide to silver. A second layer of the oxide was applied, reduced to silver, and the process repeated until the adherent silver obscured the underlying platinum wire. Three or four such bakings were sufficient. The final baking process was usually continued over night and concluded the following morning by a gradual reduction of the temperatures of the furnace in order to avoid the development of strains in the silver. Ordinarily, four electrodes were simultaneously prepared.

The silver oxide was prepared by the addition of one-tenth molal silver nitrate to one-tenth molal sodium hydroxide. The solution of silver nitrate was prepared from recrystallized silver nitrate (Baker's Analyzed) crystals and conductivity water. The solution of sodium hydroxide was prepared from Mallinkrodt's Reagent Quality sodium hydroxide and conductivity water. The precipitate was washed by frequent changes of distilled water until the wash water did not change the color of red litmus. Then, the silver oxide was shaken with conductivity water and allowed to stand for at least a week with occasional replacements by fresh conductivity water. The oxide was kept in water in a 500 cc. stoppered bottle.

The silver covered spirals were tested by comparison of the electromotive forces between them. For this purpose (Fig. 1),

four necks were made and sealed at regular intervals upon the periphery of a 500 ml. Erlenmeyer flask of Pyrex glass. These necks had inner surfaces ground to fit glass stoppers bearing the platinum wires of the spiral electrodes. A solution, prepared from conductivity water and an excess of silver chloride, completely covered the spirals. The electrodes generally differed by not more than 0.02 millivolt. Twenty-four electrodes were prepared during the progress of the experimental work and only one of them was seriously at variance with the others. This one was one of a group of four prepared simultaneously and it yielded a potential 3.5 millivolts positive with respect to the other three which varied from one another not more than 0.01 millivolt. After the group of the four electrodes had been coated with silver chloride, the faulty one was still 3.5 millivolts positive as compared with one of the other three which still agreed quite closely with one another.

By electrolysis, silver chloride was deposited upon the silver on the spiral electrode. For this purpose, two methods were tried, an older unsatisfactory method, and a new satisfactory one. The older procedure was as follows. One or more electrodes were made anode in a pure aqueous solution of hydrogen chloride. A platinum wire sealed into the end of a glass tube was made cathode. The electrolysis was carried out in a Pyrex glass beaker painted on the outside with black enamel. The electrodes and a motor driven glass stirrer were inserted in holes in a wooden lid for the beaker. A current of about four milliamperes per electrode was used, and the electrolysis was continued for about six hours.

The chief objection to this procedure is that the electrodes are often covered with a brown material instead of the

white silver chloride. Many workers have used such brown electrodes, which, as noted by Carmody¹ (and confirmed in this work), are usually about 0.2 millivolt positive with respect to the white electrodes. In an attempt to obtain white electrodes, conditions were varied. The concentration of the aqueous solution of hydrogen chloride, used as electrolyte, was varied from 0.01 to 0.75 molal without success. The use of an aqueous solution of sodium chloride appeared to reduce the proportion of white electrodes. The current was varied from one milliampere to seventy-five milliamperes per electrode without obvious reduction in the proportion of brown electrodes.

The brown electrodes were not noticeably attacked by concentrated or dilute nitric acid. But, the brown material was readily dissolved in strong aqueous ammonia, and from the resulting solution white silver chloride was precipitated upon acidification with nitric acid. MacInnes and Parker² have suggested that the brown and the white modifications of silver chloride are allotropic forms. If they are, the brown is the metastable form at 25°C. since the brown electrode is more positive than the white one.

The method finally used to deposit a layer of silver chloride upon the electrodes is as follows. Near the bottom of the electrolytic cell (Fig. 1), previously described in connection with the testing of silver coated electrodes, a platinum wire was sealed through the wall so that it could be used as a cathode. Two glass tubes for hydrogen gas, supported by a paraffined cork stopper, fit the principal neck of the flask and served as inlet and outlet for the gas. Four spiral electrodes, silver covered,

¹Loc. cit.

²Loc. cit.

were supported by the ground glass stoppers in the four smaller necks of the flask. A pure aqueous solution of hydrogen chloride, 0.01 molal, was used as the electrolyte. It was stirred by hydrogen gas generated electrolytically and passed through a wash bottle containing pure 0.01 molal hydrogen chloride solution, before it entered the electrolyzing flask. The current of four milliamperes per electrode was started 45 minutes after hydrogen had started bubbling through the solution. Then, the electrolysis was continued from 4 to 5 hours, while light was excluded from the electrolyzing flask by means of black cloth. Every electrode prepared by this procedure was perfectly white. Twenty-four such electrodes were prepared, in six preparations, four electrodes simultaneously coated in each preparation. With only one exception, mentioned in the discussion of silver coated spirals, the electrodes in any one set exhibited extreme variation not greater than 0.02 millivolt. No attempt was made to electrolyze silver-silver chloride electrodes in hydrochloric acid of the same concentration as that in which they were to be employed, because Carmody¹ had demonstrated that silver-silver chloride electrodes may be prepared in solutions of different concentration from that in which they are to be used. Carmody² also showed that deterioration of the silver-silver chloride electrodes occurred if they were allowed to stand in an aqueous solution of hydrogen chloride in the presence of air. Accordingly, long exposure of the electrodes to hydrogen chloride solution in the presence of air was avoided, although all electrodes used were washed with some of the solution in which they were to be placed in the cell for electromotive force measurements.

¹Loc. cit.

²Ibid.

The hydrogen was generated by the method of Lewis, Brighton, and Sebastian.¹ Nickel electrodes and a 10 per cent aqueous solution of sodium hydroxide were used. The hydrogen liberated by electrolysis was passed first through concentrated sulfuric acid, then through a tube containing an electrically heated platinum wire, through four saturators in succession, each initially containing solution of the same concentration as that of the solution in the cell, and finally through the cell provided at the exit with a valve to prevent entrance of air. All units of the apparatus were connected by glass or silica tubing including one graded seal. The saturators and the cell were provided with ground stoppers so that samples of solution could be withdrawn for analysis.

¹Lewis, Brighton, and Sebastian, J. Am. Chem. Soc., 39, 2245 (1917).

ADSORPTION AND THE PREPARATION OF CALIBRATION SOLUTIONS

All standard solutions of hydrogen chloride used in electromotive force measurements and in the calibration of the conductivity cell were prepared, stored, transferred and used in transparent silica containers. For the preparation of dilute standard solutions, four silica flasks with ground stoppers, two silica pipettes (a 10 cc. and a 1 cc.), and a silica funnel were used. One of the flasks (60 cc.) was used as a weighing vessel. The primary standard (Table VI) was always so concentrated that adsorption of hydrogen chloride upon the walls of its container had an entirely negligible effect upon the concentration. This was demonstrated in an elaborate series of experiments to be described later. In order to be able to weigh large enough quantities of hydrogen chloride solution to make the errors in weighing negligible, one, two or three dilutions of the primary standard were necessary. A silica flask (650 cc.) was ordinarily used to contain the secondary standard solution which was prepared by the dilution of a sample of the primary standard. The secondary standard (see Table VI) was likewise so concentrated that the effect of adsorption upon the walls of its container was shown to be negligible. To make a very dilute solution, a sample of the secondary standard solution, or in one case a tertiary, and the required conductivity water were added to a three-liter silica flask. Adsorption from some of these solutions was an important factor. Concentration changes as great as 1 per cent or more

were produced. To overcome this difficulty, two solutions in succession were prepared in the three-liter flask in the same way, from the same amounts of standard hydrogen chloride and water. The first of these solutions served to bring the inner surface of the flask into absorption equilibrium, and the second served as the standard to be used for calibration of the conductivity cell.

To clean the silica containers, they were first filled with aqua regia and allowed to stand for four hours. Then, the aqua regia was drained out, and the containers were rinsed with water, six washings with distilled water followed by eight washings with conductivity water. The containers were then filled with conductivity water and allowed to stand for at least two hours. The conductivity water was drained out and each container was rinsed twice with fresh samples of conductivity water. To dry the silica containers, they were heated over a Bunsen flame, and air was drawn through them.

Conductivity water was weighed in a one liter Pyrex volumetric flask (glass stoppered). To clean this flask the same procedure was used as that described for silica containers except that a cleaning solution made from potassium dichromate and sulfuric acid was used instead of aqua regia.

The first step in the preparation of a very dilute standard from the primary standard was the weighing of the dry clean silica weighing flask (60 cc.). Then, a sample of the primary standard hydrogen chloride solution was transferred from its container by means of a pipette into the weighing flask. To wash the clean dry pipette with the solution, two samples in succession were drawn into it and then discarded. The third sample drawn into the pipette was delivered into the weighing flask in such a way that no solution was allowed to moisten the upper part of the

inner walls of the neck of the flask; otherwise, evaporation might take place from the junction of the stopper with the surrounding inner surface of the neck. At least five grams of a sample of the solution were transferred into the weighing flask so that small errors made in the weighing process would be negligible. The weighing flask and sample of solution in it were carefully weighed. The solution was diluted in the weighing flask by the introduction of some conductivity water through the silica funnel. The conductivity water was taken from the one-liter Pyrex volumetric flask in which the water had been weighed. Then, by use of the silica funnel, the solution was drained from the weighing flask into the 650 cc. silica flask. A sample of the conductivity water from the one-liter Pyrex flask was now added to the weighing flask, shaken, and finally drained into the 650 cc. flask. This process was repeated fifteen times to make certain that all of the acid was transferred from the weighing flask and washed from the silica funnel into the 650 cc. flask. At least 400 grams of conductivity water were introduced into the 650 cc. silica flask to prepare the secondary standard. The liquid in the 650 cc. flask was allowed to stand at least two hours with occasional shaking to make sure that the solution was uniform. This solution was the secondary standard and from it a sample was taken to be diluted to prepare the third very dilute standard solution which in all but one experiment was the final one.

By means of the one-cc. pipette a calculated volume (at least 5 cc.) of secondary standard solution was transferred to the three-liter silica flask. Then, conductivity water (usually two or three liters) was added. The solution prepared volumetrically permitted adsorption upon the inner surface of the three-liter flask and prepared the surface so that it would not

appreciably change by adsorption, the concentration of a second solution to be prepared in the flask. The first solution was allowed to stand in the three-liter flask for at least three hours with occasional shaking. With some of this solution, the pipette (10 cc.) to be used to transfer liquid from the three-liter flask to the conductivity cell was filled and allowed to stand three hours. The conductivity cell was also filled with some of the solution and allowed to stand for at least three hours. The remaining portion of the solution in the three-liter flask was drained out, and either discarded or used for an electromotive force experiment in which the exact initial concentration was not needed. The three-liter flask was allowed to drain for fifteen minutes. Then, less than a gram of solution remained in the flask as determined by experiment. (A three-liter Pyrex glass flask was cleaned with dichromate cleaning solution, thoroughly rinsed and washed with distilled water, dried, cooled, and weighed. Distilled water was introduced, shaken for about two minutes. Then, the flask was drained for fifteen minutes and finally weighed.) The flask was not dried after the first solution had been drained out. The second solution was prepared in the wet flask.

The second solution was prepared from the same volumes of liquids as those used for the first, but the volumes of liquids were carefully weighed for the second because it was the final standard used to calibrate the conductivity cell, or for other purposes where a very dilute standard solution was needed. For the preparation of the final standard, the method of transfer of a sample of the secondary standard to the three-liter flask was the same as that already described for the transfer of a sample of primary standard to the 650 cc. flask for the preparation of secondary standard.

These procedures required for the preparation of very dilute standard aqueous solutions of hydrogen chloride in silica vessels were devised to eliminate errors due to adsorption revealed by the following experiments. In the beginning, some attempts were made to clean silica containers by the use of cleaning solution made from potassium dichromate and sulfuric acid. But it was extremely difficult to wash the cleaning solution from the containers with water. To test the effectiveness of the washings, conductivity water was used in one experiment and the conductances of samples of wash water were measured so that values of the conductance could be compared with that of some of the original water. After a silica flask which had been cleaned with the dichromate mixture was washed with fifteen rinsings of distilled water, and finally rinsed ten times with conductivity water, the final wash solution had a specific conductance of $1 \times 10^{-6} \text{ohm}^{-1} \text{cm.}^{-1}$; whereas, the conductance of a sample of the conductivity water had a specific conductance of $0.9 \times 10^{-6} \text{ohm}^{-1} \text{cm.}^{-1}$. No further washings with water were made, but aqua regia was allowed to stand in the flask for four hours. Then six washings with distilled water (about 150 cc. per washing) followed by eight with conductivity water were enough to free the flask from impurities which increase the conductance of conductivity water. As a final check on the effectiveness of the washings, some conductivity water was allowed to stand in the silica flask for three hours and then the conductance of a sample of the water was measured. The conductance was the same as that of the original conductivity water, namely, $0.9 \times 10^{-6} \text{ohm}^{-1} \text{cm.}^{-1}$. Dichromate cleaning solution was satisfactory to clean the Pyrex flask in which the conductivity was weighed. Five washings with distilled water followed by ten washings with conductivity water proved to be ample.

To determine the amount of washing required to remove all of the hydrogen chloride from the silica weighing flask, the following experimental procedure was used. A few milliliters of an aqueous solution of hydrogen chloride, 2.55 molal, were put into a clean dry transparent silica flask of about 60 ml. capacity and then diluted by the addition of "equilibrium" water described in the next paragraph. The solution was drained from the flask. A second portion of "equilibrium" water was introduced. The flask and contents were shaken for a short time, and the liquid drained out. The process was repeated until fifteen washings had been made. The conductances of the fifth, tenth and fifteenth samples of wash solution were measured and compared with the conductance of some of the "equilibrium" water which had not been in the flask. The data obtained in these experiments are given in Table VII.

The procedure used to prepare the so-called equilibrium water was as follows. Conductivity water was collected from the still in a two liter Pyrex bottle until the bottle was about three-fourths full. In a two-holed cork stopped for the Pyrex bottle there were two glass tubes. One tube was attached to a filter pump, the other to a wash bottle containing some conductivity water. Two other wash bottles containing concentrated sulfuric acid, the conductivity water bottle and the two-liter bottle were connected in a row so that air was forced through them in succession when the filter pump was operating. The clean air was not bubbled through the conductivity water in the Pyrex bottle, but a slow current of the air continued to flow through the bottle above the surface of the water. The specific conductance varied very little after the fourth day. (Complete equilibrium could not have been reached in this way because diffusion takes place too slowly.) This procedure was devised to produce water with definite

properties approximately equivalent to that usually described as "Equilibrium Water."

TABLE VII
SPECIFIC CONDUCTANCE OF EQUILIBRIUM WATER AND
OF WASH SOLUTIONS

(a) Specific conductance of conductivity water freshly prepared..	$0.72 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$
(b) Specific conductance of the water after it had stood in contact with clean air for two days....	$0.85 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$
(c) Specific conductance of the water after it had stood in contact with clean air for four days...	$0.916 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$
(d) Specific conductance of the water after it had stood in contact with clean air for five days...	$0.916 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$
(e) Specific conductance of the fifth wash solution.....	$2.03 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$
(f) Specific conductance of the tenth wash solution.....	$1.10 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$
(g) Specific conductance of the fifteenth wash solution.....	$0.918 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$
Cell constant.....	0.10243

These data indicate that it is necessary to rinse the small quartz flask with fifteen samples of conductivity water in order to transfer the acid from the flask completely.

The influence of adsorption upon the concentration of hydrogen chloride in an aqueous solution introduced into a clean transparent quartz flask was tested as follows. Two transparent silica flasks (one about 0.65 liter, the other 3 liters) were thoroughly cleaned (as previously described, see p. 39) and then well rinsed with "equilibrium" water. They were dried by heat and by the use of suction in the usual manner. After the 0.65

liter flask had cooled, 10 ml. of an aqueous solution of hydrogen chloride 0.0061 molar were introduced into the flask by means of a 10 ml. transparent silica pipette. Then 500 ml. of "equilibrium" water were added. The solution (approximately 0.00012 molar) formed was allowed to stand in the flask for two hours with occasional shaking. The 10 ml. quartz pipette was well cleaned, rinsed, and finally dried by heat. A sample of the hydrogen chloride solution was withdrawn from the 0.65 liter flask by means of the pipette and introduced into the quartz conductivity cell in which the solution was shaken for a minute and then drained out. In this way, the pipette and the conductivity cell were washed several times with hydrogen chloride solution before a final sample of 40 ml. was put into the cell for a conductance measurement which was made after the conductivity cell had been allowed to remain in the thermostat for thirty minutes. In the same way, and with the same apparatus, a second sample of the dilute solution (approximately 0.00012 molar) was transferred from the flask to the cell. Its conductance was higher than the conductance of the first sample. The change indicated that adsorption had altered the composition of at least the first sample. The third and fourth samples, however, yielded specific conductances in good agreement (Table VIII).

The residual solution in the 0.65 liter flask was now drained into the dry 3-liter flask. After the solution had stood in this flask for two hours with occasional shaking, the pipette and conductivity cell were washed with a succession of small amounts of that solution. Then, measurements were made with a second series of samples. There were no significant variations among the four conductances of the samples since adsorption upon the walls of the pipette and conductivity cell was not causing further changes in the concentration. The difference between the

last two values of column two and the values of column three, however, shows that the concentration was decreased about 1.4 per cent when the hydrochloric acid was poured into the three-liter flask.

A second experiment was performed like the first, except that the silica apparatus was not washed or dried. The 0.65 liter flask still wet with the solution of the preceding experiment was used for the preparation of a new solution. After the pipette and the cell had been rinsed with the newly prepared solution, a series of four conductance measurements was made (Table IX). The solution was then poured into the three-liter flask, the walls of which were still wet with the solution of the preceding experiment. The flask was shaken occasionally during a period of two hours. Samples were then pipetted from the flask and their specific conductance determined. The data which are in Table IX show that there was no appreciable concentration change.

Storage of a solution of hydrogen chloride in a silica vessel does not appreciably change the concentration after equilibrium between the solution and the containing walls has been attained. The electrical resistance of an aqueous solution of hydrogen chloride, 8.623×10^{-5} molal, remained constant for twenty-one days. On March 23, 1932, a week after the solution had been prepared, the electrical resistance of a sample of the solution was 2651.45 ohms; on March 31, 1932, the resistance of a second sample of the solution was 2651.65 ohms; on April 7, 1932, a third sample had a resistance of 2651.45 ohms; on April 14, 1932, a fourth sample gave a resistance measurement of 2651.34 ohms. The solution was stored, during the four week period, in a three-liter silica flask provided with a ground stopper.

TABLE VIII

CONDUCTANCES OF HCl SOLUTIONS REMOVED IN SUCCESSION FROM SILICA FLASKS IN WHICH ADSORPTION UPON THEIR INNER SURFACES HAD OCCURRED. INITIAL MOLALITY OF SOLUTION WAS ABOUT 1.2×10^{-5}

Sample No.	Specific Conductance (ohm ⁻¹ cm. ⁻¹) of Samples from the 0.65 Liter Flask	Specific Conductance (ohm ⁻¹ cm. ⁻¹) of Samples Removed from the 3 Liter Flask
I.	$(4.99_{41} \times 10^{-5})$	$4.89_{95} \times 10^{-5}$
II.	$(4.97_{23} \times 10^{-5})$	$4.89_{86} \times 10^{-5}$
III.	$4.96_{86} \times 10^{-5}$	$4.89_{63} \times 10^{-5}$
IV.	$4.96_{64} \times 10^{-5}$	$4.89_{63} \times 10^{-5}$

TABLE IX

CONDUCTANCE OF SAMPLES OF HCl SOLUTIONS REMOVED IN SUCCESSION FROM SILICA FLASKS IN WHICH VERY LITTLE ADSORPTION UPON THEIR INNER SURFACES OCCURRED

Sample No.	Specific Conductance (ohm ⁻¹ cm. ⁻¹) of Samples from the 0.65 Liter Flask	Specific Conductance (ohm ⁻¹ cm. ⁻¹) of Samples Removed from the 3 Liter Flask
I.	$5.09_{80} \times 10^{-5}$	$5.09_{80} \times 10^{-5}$
II.	$5.09_{76} \times 10^{-5}$	$5.09_{78} \times 10^{-5}$
III.	$5.09_{92} \times 10^{-5}$	$5.09_{75} \times 10^{-5}$
IV.	$5.09_{85} \times 10^{-5}$	$5.09_{90} \times 10^{-5}$

THE EXPERIMENTAL DETERMINATION OF ELECTROMOTIVE FORCES AND THE CORRESPONDING MOLALITIES

The electromotive force cell (Fig. 1) and the saturators were cleaned with aqua regia and washed in the same way that has already been described for the cleaning of silica containers. The cell and saturators were filled with an aqueous solution of hydrogen chloride of a concentration equal to or less than the concentration for which an electromotive force measurement was to be made. Each saturator was filled about two-thirds full of solution and the cell was filled to about the height indicated in Figure 1. The stoppers were inserted and sealed in the necks of the containers with a little paraffin. The cell and saturators were put into the oil in the thermostat at 25°C. Then, pure hydrogen was passed through the solution in the saturators and in the cell at the rate of about two liters per hour (the amount of time required for the hydrogen to fill a liter flask was determined). After hydrogen had passed through the apparatus for four or five hours, the cell reached its maximum electromotive force, except in one case (see Fig. 4). For at least five hours longer, the hydrogen flow through the apparatus was continued to make sure that all air had been displaced from the cell before the final electromotive force value was accepted. The cell contained two silver-silver chloride electrodes and one platinum electrode so that for each measurement two voltage readings were made one to three minutes apart. Several voltage measurements were always made during the ten hours or longer that hydrogen continued to bubble through the electrolyte

in the cell. The flow of hydrogen was shut off for two or three minutes, while a measurement was made, because the bubbling of hydrogen through the electrolyte produced small fluctuations in the observed voltage. The barometer was read, and the room temperature was noted at the time of each electromotive force measurement.

The most dilute solution used was prepared in the cell by the introduction of silver chloride¹ and conductivity water. In this solution, the only hydrogen and chloride ions present initially were supplied by the ionization of the water (and possibly a trace of carbonic acid) and the dissolved silver chloride. The reaction between hydrogen and silver chloride increased the $m \pm$ to 2.6×10^{-5} molal by the time the final electromotive force measurement was made (Table XII and Fig. 4). In sufficiently concentrated solutions, the rate of formation of hydrogen chloride was so small that very little voltage decrease was observed during ten to fifteen hours while hydrogen was flowing through the cell (Fig. 4).

Before the final electromotive force measurement was made, the conductivity cell was cleaned, washed and calibrated. The cell, except the electrodes and stopper, was cleaned by the use of aqua regia in the same way that the other silica containers were cleaned. After the electrodes had been prepared in the manner already described, they were allowed to stand for at least ten hours in conductivity water with occasional changings of the water. Then, the cell was filled with some of the calibration solution with which the electrodes and the cell walls were allowed

¹The Linhart electrode was put into the cell to saturate the solution with silver chloride and to make separate investigation not reported here.

to come into equilibrium for at least an hour, during which time the solution was changed at least three times. Finally, a definite volume of the calibration solution was introduced into the cell with the pipette which had been cleaned, washed, and "seasoned" with some of the calibration solution. The first measurement of the electrical resistance was made about twenty minutes after the conductance cell was placed in the thermostat and then resistance measurements were made every ten minutes until the same values were obtained in succession. Then, the cell was removed from the thermostat, drained, washed with some of the calibration solution, and finally returned to the thermostat with a second portion of calibration solution. A similar succession of resistance measurements was made on the new sample. If the second measurement differed by more than 0.01 per cent from the first, a third sample of solution was measured.

The wire cage supporting the cell in the thermostat served two purposes. It was a convenient instrument for holding the cell firmly in a reproducible position and it also supported a piece of black cambric which covered its sides and bottom. The cambric reduced the amount of light absorbed by the parts of the cell from the thermostat heating lamp, but it permitted sufficient flow of oil to keep the temperature in the cage within 0.01° of that outside.

To prevent appreciable change in the hydrogen chloride concentration after the final electromotive force measurement was made, the stoppers and electrodes were quickly removed from the electromotive force cell within two minutes following the final voltage measurement. When the stoppers were removed, no further change in the hydrogen chloride concentration occurred because no platinum remained in the cell. Samples of the residual solution

were removed from the electromotive force cell by means of the silica pipette. The first were used to wash the conductivity cell, and the final one to fill the cell for resistance measurements. The resistances of successive samples of the residual solution were measured until checks were obtained. The residual solution always had a concentration approximately the same as that of the calibration solution. The results of twelve electromotive force experiments are given in Table XII.

CALCULATION OF THE COMPOSITION OF RESIDUAL SOLUTIONS

The solution remaining in the electromotive force cell at the end of an experiment, contained hydrogen chloride, silver chloride, and water. To determine the composition, the following procedure was used. The resistance of the silica conductivity cell was carefully determined as previously described when it was filled with some of the residual solution and when it was filled with a calibration solution. The latter was carefully prepared so as to have a specific conductance approximately equal to that of the unknown (residual solution). In some experiments in which the concentration change was very small, the calibration solution was a portion of the solution originally introduced into the electromotive force cell. The specific conductance of each calibration solution was calculated by means of the following equation,¹

$$\Lambda = 426.04 - 156.7 \sqrt{C} - 165.0 C (1 - 0.2274 \sqrt{C}) \quad (1)$$

Λ is the equivalent conductance of HCl at concentration, C, expressed in moles per liter at 25°C.

It was necessary to determine the various concentrations by a method of successive approximation. The specific conductance of a residual solution in the electromotive force cell was first calculated by the use of the equation,

$$L_1 R_1 = L_2 R_2 \quad (2)$$

¹Shedlovsky, J. Am. Chem. Soc., 54, 1405 (1932).

and the first approximation to the molarity of the chloride ion by means of the equation,

$$C_1 R_1 = C_2 R_2, \quad (3)$$

C_1 , L_1 , and R_1 are the chloride ion molarity (moles per liter), specific conductance, and electrical resistance, respectively, of the calibration solution of hydrogen chloride. C_2 , L_2 , and R_2 are the corresponding values for the residual solution. The approximate molarity of the chloride ion obtained in this way was used for the calculation of the approximate activity coefficient of silver chloride, from the equation,

$$\log \gamma_{\text{AgCl}} = -.5067 \sqrt{C_2}. \quad (4)$$

This value was substituted in equation¹(5), and the approximate value of C_{AgCl} was calculated.

$$(C_{\text{Ag}^+})(C_{\text{Cl}^-})\gamma^2 = 1.617 \times 10^{-10} \quad (5)$$

Then, it was substituted in the equation,²

$$\Lambda_{\text{AgCl}} = 138.22 - 91.22\sqrt{C} + 96 C (1 - 0.2274\sqrt{C}) \quad (6)$$

and the equivalent conductance, Λ_{AgCl} , of silver chloride was calculated.

The following equation was then used to calculate the second approximation to the concentration of chloride ion.

$$(C_{\text{HCl}} \Lambda_{\text{HCl}} + C_{\text{AgCl}} \Lambda_{\text{AgCl}}) 10^{-3} = L \quad (7)$$

(The validity of this equation and the justification of this calculation procedure is discussed in the next paragraph.) Λ_{HCl} is

¹Popoff and Neuman, *J. Phys. Chem.*, 34, 1853 (1930);
Neuman, *J. Am. Chem. Soc.*, 54, 2195 (1932).

²Shedlovsky, *loc. cit.*

the equivalent conductance of hydrogen chloride in an aqueous solution in which the molarity of hydrogen chloride is the same as the total molarity of the mixture. Λ_{AgCl} is the equivalent conductance of silver chloride in an aqueous solution in which the silver chloride molarity is the total molarity of the mixture. L , found by experiment, is the specific conductance of the mixture. The value of C_{HCl} was then calculated by means of equation (1), and the new value of C , or $(C_{\text{HCl}} + C_{\text{AgCl}})$. From this approximate total Cl^- molarity, the second approximation to the activity coefficient of the silver chloride was obtained by means of equation (4). Then, the calculation procedure was repeated until two successive values for the molarity of hydrogen ion in the residual solution, obtained by two successive calculations, were equal.

Smith and Gortner¹ have recently tested the validity of equation (7), and have summarized the work of others. They found only slight deviations from it, using concentrations as high as 0.01 normal. Furthermore, three experiments were performed in this investigation to obtain evidence which supports equation (7). The experiments were alike except that solutions of different concentration were used. In each experiment, a solution of hydrogen chloride was introduced into the saturators and into the electromotive force cell. In order to prevent the side reaction (p. 12), no platinum was exposed to the solution. The cell and saturators were put into the thermostat at 25°C. After they had remained in the thermostat for four hours, the electrical resistance of a sample of the solution removed from the cell was measured one hour later to determine whether the solution had come

¹Smith and Gortner, J. Phys. Chem., 37, 79 (1933).

into equilibrium with the surfaces of the quartz. Hydrogen gas, prepared as described previously, was then passed through the saturators and through the cell for two days. The resistance of a sample of the residual solution taken from the cell was measured in order to show whether any change in resistance had been produced by the hydrogen. A little carbon dioxide, for example, might be removed. Then, a little silver chloride, which had been standing in some hydrochloric acid of the same concentration as that initially used in the experiment, was introduced into the residual solution in the cell. Hydrogen was again passed through the cell for two days. At the end of the two day period, the resistance of a sample of the solution saturated with silver chloride was measured.

The results obtained in this way in three different experiments are given in Table X. In the case of the most dilute HCl solution, about 2.9×10^{-5} molal, the specific conductance decreased about 1 per cent because of adsorption of hydrogen chloride upon the surface of the silica container. The adsorption was complete at the end of four hours (Table X, 2, 4, and 5). The passage of hydrogen for two days through the hydrogen chloride solution, initially about 2.9×10^{-5} molal, reduced the specific conductance of the solution by 0.16 per cent. This is probably due to removal of carbon dioxide (Table X, 5 and 6). There was no change in the resistance of the solution containing hydrogen chloride and silver chloride when hydrogen passed through the solution for two days in the absence of platinum (Table X, 7 and 8). There was good agreement between the experimental and calculated values of the specific conductances of mixtures of hydrogen chloride and silver chloride (Table X, 10 and 11).

In another experiment, the specific conductance of some

TABLE X

EFFECT OF AgCl AND OF CO₂ UPON SPECIFIC CONDUCTANCE
OF HCl SOLUTIONS

		Solution I	Solution II	Solution III
1	Molality of HCl solution used to calibrate conductivity cell	$2.925_5 \times 10^{-5}$	$2.515_2 \times 10^{-4}$	$3.022_6 \times 10^{-3}$
2	Specific conductance of the calibration solution used to calibrate conductivity cell	$1.241_8 \times 10^{-5}$	$1.064_9 \times 10^{-4}$	$1.260_9 \times 10^{-3}$
3	Cell constant	0.1555_{34}	0.1027_{11}	0.2010_6
4	Specific conductance of HCl solution after it had stood for four hours in the E. M. F. cell	$1.226_{85} \times 10^{-5}$	$1.060_2 \times 10^{-4}$	$1.260_9 \times 10^{-3}$
5	Specific conductance of HCl solution after it had stood for five hours in the E. M. F. cell	$1.226_{85} \times 10^{-5}$	$1.060_2 \times 10^{-4}$	$1.260_9 \times 10^{-3}$
6	Specific conductance of HCl solution after H ₂ had passed through it for two days	$1.224_{92} \times 10^{-5}$	$1.059_8 \times 10^{-4}$	$1.260_9 \times 10^{-3}$
7	Specific conductance of solution after AgCl had been added and H ₂ had passed through solution for two days	$1.293_{71} \times 10^{-5}$	$1.060_7 \times 10^{-4}$	$1.260_9 \times 10^{-3}$
8	Specific conductance after AgCl had been added and H ₂ had passed through the solution for four days	$1.293_{67} \times 10^{-5}$	$1.060_7 \times 10^{-4}$	$1.260_9 \times 10^{-3}$

TABLE X--CONTINUED

		Solution I	Solution II	Solution III
9	Concentration of Ag^+ in moles per liter in HCl solution (calculated from data of Popoff)	$0.4873_2 \times 10^{-5}$	$0.6757_4 \times 10^{-6}$	$0.6094_7 \times 10^{-7}$
10	Observed specific conductance of AgCl dissolved in HCl solution (the change in the specific conductance, or the difference between the value No. 6 and the value No. 7 above)	$0.068_{79} \times 10^{-5}$	$0.0093_0 \times 10^{-5}$	0.000
11	Specific conductance of dissolved AgCl (calculated from equation of Shedlovsky)	$0.066_{91} \times 10^{-5}$	$0.0093_0 \times 10^{-5}$	0.00084×10^{-5}
12	Per cent difference between calculated and experimental values of specific conductance for HCl-AgCl solution (Series 8 and 11 of this table)	0.15	0.000	0.000
13	Per cent change in molality that occurred when H_2 passed through solution for two days (CO_2 removal)	0.16	0.04	0.000

freshly prepared conductivity water was measured. Some of the conductivity water which had been exposed to clean air (see method on p. 43) was introduced into the electromotive force cell and saturators. During this treatment of the water, its specific

conductance rose presumably because of exposure to the air. In a similar experiment, an aqueous solution of an acid was used in the same way. Hydrogen was passed through each liquid for six hours. Successive samples of each liquid were allowed to come into equilibrium with the inner surfaces of the conductivity cell, until successive resistance measurements yielded the same results. The data are given in Table XI.

In six hours, the specific conductance of the hydrogen chloride solution was decreased 0.085 per cent as hydrogen continued to pass through the solution in the cell. This result appears to indicate that a longer period than six hours is needed to reduce the carbon dioxide concentration to an amount too small to be detected by conductance measurements; for in a former experiment (see Table X) it was noted that the flow of hydrogen for two days through a solution, initially 2.9×10^{-5} molal, reduced the specific conductance 0.16 per cent. When conductivity water was used in lieu of an acid solution in the cell and saturators, the specific conductance was lowered by the hydrogen in six hours to a little less than the original value.

The carbon dioxide from the air is a source of error in the electromotive force and conductance measurements for hydrogen chloride solutions so dilute that dissolved carbon dioxide can be detected. The calibration solutions were made from water that had been in contact with the air. Carbon dioxide was probably removed from the solution in the electromotive force cell by the hydrogen which continually passed through it until the final electromotive force measurement was made. The sample of residual solution removed from the electromotive force cell for the conductance measurement, however, undoubtedly absorbed some carbon dioxide before its conductance was measured. If this sample of solution had come

TABLE XI

THE REMOVAL OF CO₂ FROM LIQUIDS BY H₂
DURING SIX HOURS

Type of Liquid	Initial Specific Conductance of Conductance of Water Freshly Prepared	Specific Conductance of Calibration Liquid after it Has Come Into Absorption Equilibrium in the Cell	Specific Conductance of Residual Liquid after H ₂ Has Passed Through for Six Hours	Initial Molality of HCl Solution	Apparent Molality of Residual Solution
HCl Soln.	0.652x10 ⁻⁶ *	1.220x10 ⁻⁵	1.219x10 ⁻⁵	2.876x10 ⁻⁵	2.873x10 ⁻⁵
Cond. H ₂ O	0.616x10 ⁻⁶	0.875x10 ⁻⁶	0.590x10 ⁻⁶		

*Specific conductance of water used to prepare the HCl solution, 2.876x10⁻⁵ molal.

into equilibrium with the air before its resistance was measured and if nearly all of the carbon dioxide had been removed by the flow of hydrogen before the final electromotive force measurement was made, the error due to carbon dioxide would have been reduced to zero.

The maximum error due to carbon dioxide that could be introduced into the results reported herewith was calculated as follows. The equilibrium constant¹ for the primary ionization of carbon dioxide in aqueous solution at 25°C. is 4.54×10^{-7} . The limiting equivalent conductance² of carbon dioxide in aqueous solution at 25°C. is 396.6 ohm^{-1} . The specific conductance of the conductivity water used to prepare standard solutions of hydrogen chloride was $0.9 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$. The concentration of H^+ and of HCO_3^- formed from the carbon dioxide, was calculated by use of the equation,

$$(\text{HCO}_3^-) = \frac{1000 \times 0.9 \times 10^{-6}}{396.6} = 2.269 \times 10^{-6} \quad (1)$$

$$\text{Then,} \quad (\text{H}_2\text{CO}_3) = \frac{(2.269 \times 10^{-6})^2}{4.54 \times 10^{-7}} = 1.134 \times 10^{-5} \quad (2)$$

The total concentration of H_2CO_3 is $(\text{HCO}_3^-) + (\text{H}_2\text{CO}_3)$, or 1.36×10^{-5} . When (H^+) is 2.6332×10^{-5} , which is the molarity of the most dilute solution for which an electromotive force measurement was made, the (H^+) in the solution containing carbon dioxide is calculated from the following equations.

$$\frac{[2.6332 \times 10^{-5} + (\text{HCO}_3^-)] (\text{HCO}_3^-)}{(\text{H}_2\text{CO}_3)} = 4.54 \times 10^{-7} \quad (3)$$

¹MacInnes and Belcher, J. Am. Chem. Soc., 55, 2630 (1933).

²International Critical Tables, McGraw-Hill Book Co., New York, Vol. VI, 1929, p. 261.

The first approximation is obtained from,

$$(\text{HCO}_3^-) = \frac{(4.54 \times 10^{-7})(1.361 \times 10^{-5})}{2.6332 \times 10^{-5}} = 2.3465 \times 10^{-7} \quad (4)$$

$$\text{and } (\text{H}^+) = 2.6332 \times 10^{-5} + 0.02346 \times 10^{-5} = 2.6566 \times 10^{-5} \quad (5)$$

The second approximation was then obtained as follows:

$$(\text{H}_2\text{CO}_3) = 1.361 \times 10^{-5} - 2.3 \times 10^{-7} = 1.338 \times 10^{-5}, \quad (6)$$

$$\text{and } (\text{HCO}_3^-) = \frac{4.54 \times 10^{-7} \times 1.338 \times 10^{-5}}{2.6566 \times 10^{-5}} = 2.285 \times 10^{-7} \quad (7)$$

$$(\text{H}^+) = 2.6332 \times 10^{-5} + 2.285 \times 10^{-7} = 2.6560 \times 10^{-5}$$

Thus, (H^+) from the H_2CO_3 amounts to 0.86 per cent of the HCl molarity. This corresponds to 0.4 millivolt under the most unfavorable circumstances, namely, if the residual solution retains no carbon dioxide and if no carbon dioxide is absorbed before its resistance is measured. This estimate is for the most dilute solution used to obtain electromotive force data (Table XII). The error in the next most dilute solution could be only one-fourth as great.

The actual error is undoubtedly smaller than the maximum possible error. In the first place, the calculated carbon dioxide is undoubtedly too large because part of the conductance was due to impurities such as dissolved materials from the Pyrex glass bottles in which the conductivity water was collected. These impurities imparted conductance to the solutions. In fact, according to the results given in Table XI, these impurities furnished about two-thirds of the total conductance of the conductivity water. Accordingly, the specific conductance due to carbon dioxide amounted to about $0.3 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$. This corresponds to the

maximum possible error of about 0.28 per cent in the molarity (2.6×10^{-5}) of the most dilute residual solution and the maximum error in the electromotive force measurement would amount to about 0.15 millivolt. In the second place, there was undoubtedly some carbon dioxide absorption by the residual solution before its resistance measurement was made and the error would therefore be less than 0.15 millivolt. It is not probable that the actual error is as great as 0.1 millivolt. If it even approaches this figure, there must have been some compensating error because the last point lies very close to the theoretical curve. One of the experiments performed in the investigation of the effects of carbon dioxide (Table X) was made with a solution about 2.9×10^{-5} molal, and the change in specific conductance due to carbon dioxide removal was 0.16 per cent. This corresponds to an error of about 0.1 millivolt for a 2.6×10^{-5} molal solution. Since the error in electromotive force is inversely proportional to the square of molality of the solution, no point (Fig. 4) other than the last could have been affected seriously.

THE CALCULATION OF E, THE CORRECTED ELECTROMOTIVE FORCE

Electromotive force measurements reported in the literature have been made, for the most part, with hydrogen chloride solutions sufficiently concentrated to render corrections for dissolved silver chloride nearly or entirely negligible. The correction for Carmody's¹ most dilute solution (0.0003288 molal) was only 0.39 millivolt. Linhart² has reported a value of an electromotive force for a solution (0.000136 molal).³ The correction for dissolved silver chloride reported by Linhart for his most dilute solution was 0.3 millivolt. He accepted 2.4×10^{-10} as the best value available at that time for the solubility product of silver chloride, and calculated the value of the voltage correction from the equations,

$$(\text{Ag}^+)(\text{Cl}^-)' = 2.4 \times 10^{-10}, \text{ and} \quad (8)$$

$$E_{(\text{Cl}^-)''} - E_{(\text{Cl}^-)'} = 0.05915 \log \frac{(\text{Cl}^-)''}{(\text{Cl}^-)'} \quad (9)$$

$(\text{Cl}^-)'$ is equal to the chloride ion concentration in pure hydrochloric acid introduced into the cell and $(\text{Cl}^-)''$ is the sum of the original chloride ion concentration and the increase due to dissolved silver chloride. A better calculation procedure is

¹Loc. cit.

²Loc. cit.

³Nonhebel (loc. cit.) has reported a value for a solution 0.0001182 molal, and he corrected for dissolved AgCl in the same way that Linhart did.

that described on pages 52-54 which involves the use of equation (2), page 52. This procedure and Popoff's¹ new value of the activity product constant results in a correction of 0.23 millivolt. At lower concentrations, the two procedures yield much greater differences. For example, when the molality of hydrogen chloride is 2.641×10^{-5} , the smallest concentration for which an electromotive force was obtained in this investigation, the value of the voltage correction obtained by Linhart's method is 7.59 millivolts; whereas, the other procedure yields the value 4.62 millivolts. The corrections for solutions as dilute as these are important and could not have been made until the investigation of Popoff² was completed.

General Equation

The following equation shows the various corrections applied to the instrument reading of the electromotive force:

$$E = E_R + \Delta E_C + \Delta E_{H_2} + \Delta E_{Ag^+} \quad (10)$$

E is the tabulated corrected value. E_R is the instrument reading. ΔE_C is the sum of two corrections: (1) a correction for the calibration values of the potentiometer coils and drum wire; (2) a correction for the Bureau of Standards calibration of the standard cell. ΔE_{H_2} is the correction for the partial pressure of hydrogen to one atmosphere. ΔE_{Ag^+} is the correction for the silver ion furnished to the solution by the silver chloride. The numerical values of all of these corrections are given in Table XII.

¹Loc. cit.

²Ibid.

The Correction ΔE_C

The potentiometer calibration has already been described (page 20). There were two standard cell corrections; one for temperature (the standard cell was not in a thermostat), the other for the fact that the electromotive force of the standard cell was tentatively accepted as 1.0189₂ volts for all of the electromotive force data of Table XII, except two, and for these two, the value tentatively accepted was 1.0188₁ volts. The electromotive force of the standard cell reported by the United States Bureau of Standards was 1.0188₅ volts, September 9, 1933. It was found by experiment that the electromotive force of an Eppley cell decreased about 0.016 millivolts per degree centigrade when the temperature increases.

The Correction of the Partial Pressure of H₂

The equation used to correct the pressure of hydrogen to one atmosphere is:

$$\Delta E_{H_2} = 0.02958 \log \frac{760}{P_{H_2}} \quad (11)$$

ΔE_{H_2} is the difference between the electromotive force of a cell Pt, H₂, HCl(xm), AgCl, Ag, when the pressure of H₂ in the cell is 760 mm. and the electromotive force of the same cell, when the partial pressure of the H₂ is P_{H_2} . P_{H_2} was obtained from the observed barometer reading by use of the equation,

$$P_{H_2} = P_0 + P_I - P_T + P_H - P_{H_2O} \quad (12)$$

P_0 is the observed barometer reading. P_I is -1.144 mm., the instrument correction for the barometer. P_T is the temperature

correction for the barometer reading. P_H is the pressure (0.5 mm.) of mercury in the exit tube from the electromotive force cell. P_{H_2O} is 23.756 mm.,¹ the vapor pressure of water at 25°C.

The Correction for the Difference
Between μ and $m \pm$

It is necessary to consider a correction for the small difference between the ionic strength,² μ , and the mean molality,³ $m \pm$. The activity coefficient, γ , is determined by μ and not by $m \pm$. It will be shown later that the data obtained in this investigation are in accord with the Debye-Hückel limiting law,

$$E^{o'} - E^o = 0.118306 \log \gamma = 0.05986 \sqrt{\mu} \quad (13)$$

The correction is therefore,

$$-0.05986 (\sqrt{\mu} - \sqrt{m \pm}).$$

This quantity was calculated for each measurement and is tabulated in Table XII, column 3, page 69. The correction in no case is significant.

¹International Critical Tables, McGraw-Hill Book Co., Inc., New York, Vol. III, 1928, p. 212.

²Lewis and Randall, op. cit., p. 373.

³Ibid., p. 329.

TABLE XII

ELECTROMOTIVE FORCE AND CORRECTIONS

T=25°C.

No. of Exp.	Date When Observation Was Made	E Uncor- rected	Standard Cell Correc- tions	Correc- tions for Calibra- tion of Potenti- ometer	E Observed (Cor- rected)
1	Aug. 22, 1933 7:12 P.M.	0.52386 ₅	+0.000035	+0.000047	0.52394 ₇
2	Aug. 23, 1933 6:30 P.M.	0.54466 ₀	+0.000022	+0.000063	0.54474 ₅
3	Aug. 14, 1933 9:24 P.M.	0.56734 ₀	+0.000018	+0.000086	0.56744 ₄
4	Aug. 24, 1933 7:45 P.M.	0.58377 ₀	+0.000028	+0.000102	0.58390 ₀
5	July 21, 1933 10:00 P.M.	0.59407 ₀	+0.000029	+0.000106	0.59420 ₅
6	Aug. 4, 1933 8:31 P.M.	0.62380 ₅	+0.000030	+0.000047	0.62388 ₂
7	Dec. 22, 1932 5:36 P.M.	0.65383 ₀	-0.000044	+0.000073	0.65385 ₉
8	July 15, 1933 7:00 P.M.	0.67982 ₀	+0.000024	+0.000100	0.67994 ₄
9	July 7, 1933 7:02 P.M.	0.69834 ₅	-0.000023	+0.000109	0.69843 ₁
10	July 18, 1933 8:48 P.M.	0.72022 ₀	+0.000009	+0.000039	0.72026 ₈
11	Feb. 9, 1933 9:22 P.M.	0.72708 ₅	-0.000020	+0.000049	0.72711 ₄
12	July 13, 1933 3:39 P.M.	0.75879 ₅	-0.000005	+0.000079	0.75886 ₉

TABLE XII--CONTINUED

ELECTROMOTIVE FORCE AND CORRECTIONS

T=25°C.

No. of Exp.	Correction for Partial Pressure of H ₂ to One Atmosphere	Correction for the Difference Between $\sqrt{m\pm}$ and μ	E Corrected for H ₂ to One Atmosphere and for $\sqrt{\mu}$ $-\sqrt{m\pm}$
1	0.000609	0.000000	0.52455 ₆
2	0.000669	0.000000	0.54541 ₄
3	0.000685	0.000000	0.56812 ₉
4	0.000738	0.000000	0.58463 ₈
5	0.000638	0.000000	0.59484 ₃
6	0.000628	0.000000	0.62451 ₀
7	0.000508	-0.000001	0.65436 ₆
8	0.000711	-0.000002	0.68065 ₃
9	0.000709	-0.000003	0.69913 ₇
10	0.000698	-0.000005	0.72096 ₁
11	0.000483	-0.000006	0.72759 ₁
12	0.000697	-0.000015	0.75955 ₁

TABLE XII--CONTINUED
PRESSURE AND CORRECTIONS

No. of Exp.	Barometer Reading in mm.	Temp. of the Baro- meter in Degrees Centigrade	Temp. Cor- rection of Baro- meter Reading in mm.	Partial Pressure of H ₂ in mm.
1	752.1	23.8	-2.9 ₁₂	724.7 ₈₈
2	748.9	25.5	-3.0 ₉₅	721.4 ₀₅
3	748.1	26.0	-3.1 ₆₂	720.5 ₃₈
4	745.0	25.0	-3.0 ₃₀	717.5 ₇₀
5	750.6	25.0	-3.0 ₅₂	723.1 ₅₀
6	751.2	25.0	-3.0 ₅₅	723.7 ₄₅
7	758.1	25.6	-3.1 ₅₄	730.5 ₄₆
8	746.6	25.8	-3.1 ₃₂	719.0 ₆₈
9	747.2	30.0	-3.6 ₄₆	719.1 ₅₄
10	747.5	27.2	-3.3 ₀₄	719.7 ₉₆
11	759.2	23.0	-2.8 ₃₈	731.9 ₆₂
12	747.7	28.5	-3.4 ₆₁	719.8 ₃₉

Height of liquid column in exit tube = 6.8 mm.

Mercury equivalent of height of liquid column = 0.5 mm.

Instrument correction (barometer) = -1.144 mm.

Vapor pressure of water at 25°C. = 23.756 mm (Int. Crit.

Tables, Vol. III, loc. cit.).

TABLE XII--CONTINUED
COMPOSITION OF SOLUTIONS

No. of Exp.	Initial Molality of HCl Solution	Calibration Molality of HCl Solution	Ratio of Resistance of Calibration Solution to the Resistance of the Residual Solution
1	$2.950_8 \times 10^{-3}$	$2.950_8 \times 10^{-3}$	1.00000 ₀
2	$1.945_8 \times 10^{-3}$	$1.945_8 \times 10^{-3}$	1.00015 ₉₉
3	$1.235_7 \times 10^{-3}$	$1.208_7 \times 10^{-3}$	1.02317 ₈₅
4	$8.923_2 \times 10^{-4}$	$8.947_6 \times 10^{-4}$	0.99968 ₀
5	$7.296_8 \times 10^{-4}$	$7.209_7 \times 10^{-4}$	1.01287 ₂
6	$4.056_4 \times 10^{-4}$	$3.874_2 \times 10^{-4}$	1.04904 ₅₆
7	$2.191_2 \times 10^{-4}$	$2.236_7 \times 10^{-4}$	1.00978 ₈
8	$1.211_5 \times 10^{-6}$	$1.398_7 \times 10^{-4}$	0.96564 ₂
9	$7.751_0 \times 10^{-5}$	$9.540_7 \times 10^{-5}$	0.98388 ₄
10	$4.789_0 \times 10^{-5}$	$6.053_4 \times 10^{-5}$	1.00677 ₃
11	$4.533_2 \times 10^{-5}$	$5.119_2 \times 10^{-5}$	1.04333 ₁₆
12	Conductivity water	$2.963_2 \times 10^{-5}$	0.94815 ₆

TABLE XII--CONTINUED
COMPOSITION OF SOLUTIONS

No. of Exp.	m Molality of HCl in Residual Solution	Molality of AgCl in the Residual Solution	Ionic Strength	Mean Molality
1	$2.950_8 \times 10^{-3}$	0.5510×10^{-7}	$2.950_9 \times 10^{-3}$	$2.950_9 \times 10^{-3}$
2	$1.946_1 \times 10^{-3}$	$.9151 \times 10^{-7}$	$1.946_2 \times 10^{-3}$	$1.946_1 \times 10^{-3}$
3	$1.236_7 \times 10^{-3}$	$.1314 \times 10^{-6}$	$1.236_8 \times 10^{-3}$	$1.236_8 \times 10^{-3}$
4	$8.944_1 \times 10^{-4}$	$.1962 \times 10^{-6}$	$8.946_1 \times 10^{-4}$	$8.945_1 \times 10^{-4}$
5	$7.301_7 \times 10^{-4}$	$.2396 \times 10^{-6}$	$7.304_1 \times 10^{-4}$	$7.302_9 \times 10^{-4}$
6	$4.062_9 \times 10^{-4}$	$.4219 \times 10^{-6}$	$4.067_1 \times 10^{-4}$	$4.065_0 \times 10^{-4}$
7	$2.256_2 \times 10^{-4}$	$.7478 \times 10^{-6}$	$2.263_7 \times 10^{-4}$	$2.259_9 \times 10^{-4}$
8	$1.346_7 \times 10^{-4}$	$.1235 \times 10^{-5}$	$1.359_0 \times 10^{-4}$	$1.352_8 \times 10^{-4}$
9	$9.330_1 \times 10^{-5}$	$.1756 \times 10^{-5}$	$9.505_7 \times 10^{-5}$	$9.417_5 \times 10^{-5}$
10	$6.008_8 \times 10^{-5}$	$.2647 \times 10^{-5}$	$6.273_5 \times 10^{-5}$	$6.139_7 \times 10^{-5}$
11	$5.244_3 \times 10^{-5}$	$.2992 \times 10^{-5}$	$5.543_5 \times 10^{-5}$	$5.391_8 \times 10^{-5}$
12	$2.640_9 \times 10^{-5}$	0.5219×10^{-5}	$3.162_8 \times 10^{-5}$	$2.890_1 \times 10^{-5}$

TABLE XII--CONTINUED
DATA FOR CURVES IN FIGURE 4

No. of Exp.	$\sqrt{\mu}$	$\sqrt{mF}$	E^0 (Ob- served)	E^0 (Calcu- lated)	$E^0_{\text{obs.}} - E^0_{\text{calc.}}$ or $E_{\text{obs.}} - E_{\text{calc.}}$
1	0.5432 ₂	0.5432 ₂	0.22522 ₉	0.22521 ₈	+0.00001 ₁
2	.04411 ₆	.04411 ₅	.22470 ₀	.22468 ₈	+ .00001 ₂
3	.03516 ₉	.03516 ₈	.22412 ₄	.22421 ₀	- .00008 ₆
4	.02991 ₀	.02990 ₈	.22398 ₆	.22392 ₃	+ .00006 ₃
5	.02702 ₇	.02704 ₀	.22377 ₀	.22376 ₅	+ .00000 ₅
6	.02016 ₇	.02016 ₂	.22333 ₅	.22337 ₉	- .00004 ₄
7	.01504 ₅	.01503 ₃	.22302 ₆	.22308 ₇	- .00006 ₁
8	.01165 ₈	.01163 ₁	.22294 ₈	.22289 ₀	+ .00005 ₈
9	.009749 ₇	.009704 ₄	.22282 ₁	.22277 ₇	+ .00004 ₄
10	.007820 ₅	.007835 ₆	.22266 ₆	.22266 ₉	- .00000 ₃
11	.007445 ₅	.007342 ₉	.22262 ₂	.22264 ₀	- .00001 ₈
12.	0.005623 ₉	0.005376 ₀	0.22254 ₁	0.22252 ₅	+0.00001 ₆

DISCUSSION OF RESULTS

The value of E^0' corresponding to each molality, was calculated by use of the equation,¹

$$E^{0'} = E - 0.1183_{08} \log m_{\pm} = E^0 - 0.1183_{08} \log \gamma \quad (14)$$

E is the corrected electromotive force and $m_{\pm}$ is the mean molality. The values of $E^{0'}$ were plotted against $\sqrt{m_{\pm}}$, Figure 4. For comparison, the data of Carmody² were also plotted.

According to the theory of Debye and Hückel,³ as $\mu \rightarrow 0$ (for a uni-univalent electrolyte) the ratio $\frac{2.3026 \log \gamma}{\sqrt{\mu}}$ approaches a limit,

$$\sqrt{2} \quad A \equiv \sqrt{2} \quad \sqrt{\frac{\pi N e^6}{1000 k^3 D^3 T^3}} \quad (15)$$

in which N is avogadro's number; e , the electronic charge; k , Boltzman's constant; D , the dielectric constant of the solvent; and T , the absolute temperature. According to Birge's⁴ estimates of the fundamental constants, and the more recent value of the dielectric constant obtained by Wyman,⁵ A has the value 0.823₅ at 25°C. The Debye-Hückel limiting law may therefore be written,

$$\log \gamma = -0.506 \sqrt{m}, \quad (16)$$

¹Lewis and Randall, op. cit., p. 334.

²Loc. cit.

³Loc. cit.

⁴R. T. Birge, The Physical Review Supplement, I, 1 (1929).

⁵Wyman, Phys. Rev. 35, 623 (1930).

or

$$E^0' - E^0 = (0.118308)(0.506) \sqrt{m}. \quad (17)$$

The constant 0.118308 was determined from the fundamental constants recommended by Birge and listed in Table XIII. The values earlier adopted by Lewis and Randall are also in Table XII. They lead to the value 0.118305. (Lewis and Randall used 0.11830.)

TABLE XIII
COMPARISON OF CONSTANTS AND THE EVALUATION OF
 $2.302585 \frac{NRT}{nF}$ AT 25° C.

	Normal Atmosphere	Abso- lute Temper- ature of Ice Point	The Faraday	Volume of Perfect Gas at 0°C.	R
Lewis and Randall*	1013300 dyne per sq. cm.	273.1°	96494 cou- lomb per equivalent	22.412×10^3 cm. ³ mole ⁻¹	8.315 ₆₆ joule deg. ⁻¹ mole ⁻¹
R. T. Birge**	1013249 dyne per sq. cm.	273.18°	96494 int. coulomb per equiv.	22.4141×10^3 cm. ³ mole ⁻¹	8.313 ₅₉ joule deg. ⁻¹ mole ⁻¹

*Lewis and Randall, op. cit.

**Loc. cit.

Over a wider range of concentration the theory predicts equations which may be reduced to the forms,¹

$$\log \gamma = -0.506 \sqrt{m} - Bm \quad (18)$$

¹Scatchard, J. Am. Chem. Soc., 47, 648 (1925).

and

$$E^{\circ'} = E^{\circ} - (0.118308)(0.506) \sqrt{m} - 0.118308 Bm \quad (19)$$

The constant, B, is determined by the properties of each individual electrolyte. Equation (19) may therefore be considered to have two adjustable (i.e., empirical) constants, E° and B. These two empirical constants, determined from the experimental data yielded the following empirical equation, which reduces as $m \rightarrow 0$ to the Debye-Hückel limiting law,

$$E = E^{\circ} - 0.118308 \log m - 0.0598_6 \sqrt{m} - 0.081 m \quad (20)$$

The solid line in Figure 4 represents these equations from which the calculated values of $E^{\circ'}$ in Table XII were determined. Differences between the experimental and the calculated values are also exhibited in Table XII, and are plotted in the lower portion of Figure 4. Obviously, the limiting law of Debye-Hückel is in excellent agreement with the experimental data. The disagreement noted earlier by Nonhebel¹ was due to experimental inaccuracies in some of the earlier data:

Figure 4 shows a small systematic difference between the data of Carmody and the new data obtained in this research. The difference (0.00004 volt) may have been produced by a number of possible errors. The most important is probably the uncertainty in the calibration of the standard cell by the United States Bureau of Standards. This was certified to 0.01 per cent, an error which would have produced a change of 0.00007 volt in the measurement for the most dilute solution. The agreement between the two series of results is therefore fortuitous. (Carmody expressed

¹Nonhebel, Phil. Mag. (1) 2, 1085 (1926); cf. Randall and Young, loc. cit., and Davies, loc. cit.

his voltages to 0.0001 volt only.)

The molal electrode potential of the silver-silver chloride electrodes as determined by the extrapolation of $E^{0'}$ to $\sqrt{m} = 0$, is the first term of equation (20). It is 0.2222₀ volt, in excellent agreement with Spencer's¹ interpretation of Carmody's data.

Equation (20) may be modified to yield the activity coefficient of hydrogen chloride,

$$\log \gamma = -0.506\sqrt{m} - 0.68_5 m \quad (21)$$

This equation in agreement with the Debye-Hückel limiting law yields the following typical values:

<u>m</u>	<u>γ</u>
.0005	.975 ₆
.001	.965 ₃
.002	.952 ₃

These may be employed in connection with other electromotive force data to yield coefficients for higher concentrations. Experimental work with more concentrated solutions is much less difficult. This work, therefore, establishes a reference point for the determination of other activity coefficients of hydrogen chloride.

¹Spencer, J. Am. Chem. Soc., 54, 3647 (1932).

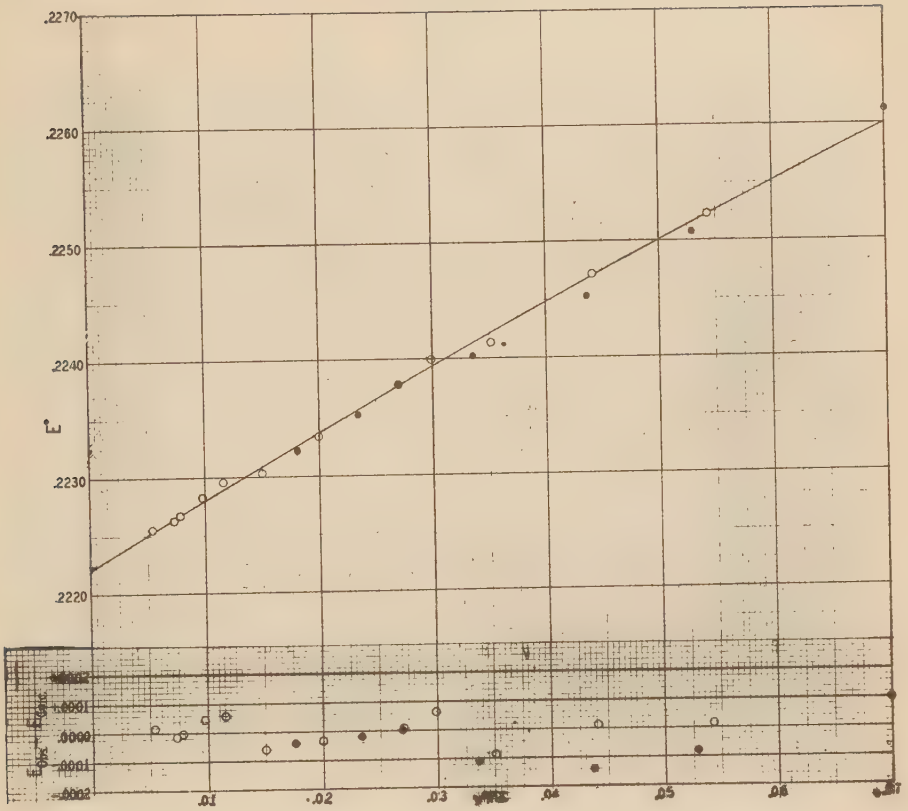


FIGURE 3

The circles represent values obtained in this investigation; the dots, values obtained by Carmody.

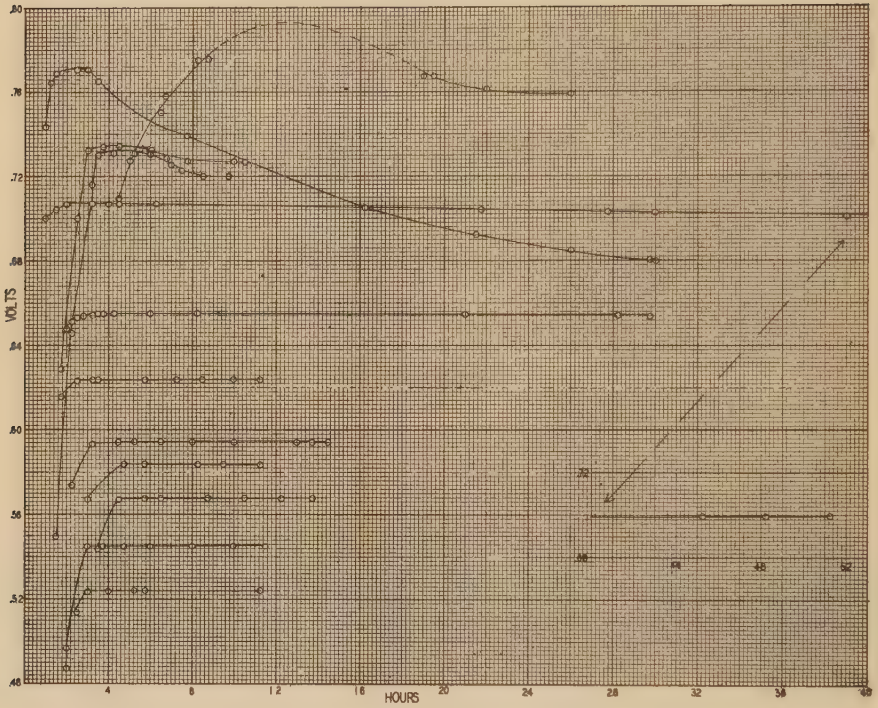


FIGURE 4

Time Variation of Voltage

The final electromotive force represents on each curve the value given in Table XIII.

SUMMARY

1. The cause of the variation of the electromotive force of the cell, Pt, H₂, HCl, AgCl, Ag, was found to be the side-reaction represented by the equation:



Concordant results for the amount of hydrogen chloride formed in this reaction could be obtained from an electromotive force measurement, from the conductance of the residual solution, and from the amount of silver deposited upon the platinum black electrode.

2. A cell, similar in some respects to the one described by Linhart, was used for electromotive force measurements. A technique was developed for the preparation of perfectly white silver-silver chloride electrodes. The concentration of the hydrogen chloride could not be determined from the analysis of the solution originally put into the cell because of the side reaction mentioned above and because of adsorption. It was determined from the conductance of the solution in the cell when the final electromotive force measurement was made. The conductance permitted the calculation of the concentration of both the hydrogen chloride and the silver chloride.

3. Reliable values of the electromotive force, in accord with the theory of Debye and Hückel, have been obtained for aqueous solutions of hydrogen chloride ranging in concentration from 2.95×10^{-3} to 2.64×10^{-5} molal. In the most dilute solution, the silver ion concentration was about 20 per cent of the hydrogen

chloride concentration.

4. Early work indicated that the Debye-Hückel theory was not applicable to aqueous solutions of hydrogen chloride, but Carmody's¹ recent results are in agreement with the theory. The data here reported are in agreement with those of Carmody,² and extend to a much higher dilution than he attempted to employ. The two series (having overlapping concentration ranges) constitute a beautiful confirmation of the theory, and permit precise evaluation of the activity coefficients.

5. The molal electrode potential, E^0 , of the silver-silver chloride electrode was found to be 0.2222₀ volt.

¹Loc. cit.

²Ibid.

